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Identification and Description of Chemical Deactivation/Detoxification Methods for the Safe Disposal of Selected Pesticides

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IDENTIFICATION AND DESCRIPTION
OF CHEMICAL DEACTIVATION/DETOXIFICATION METHODS
FOR THE SAFE DISPOSAL OF SELECTED PESTICIDES

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This sequel to the Handbook for Pesticide Disposal by Common Chemical Methods has examined chemical detoxification/degradation methods for 40 pesticides. The objectives for this study are the same as described in the companion: to develop practical chemical methods by which the layman can detoxify pesticides and to delineate hazards associated with the detoxification methods. The 40 pesticides were selected on the basis of their toxicological properties, their consumption, and their representation of other pesticides. Chemistry was reviewed for each through literature search and personal contacts with pesticide manufacturers and other sources. Although many of the selected pesticides are susceptible to alkaline hydrolysis, this approach is only recommended for 11 of the pesticides: monocrotophos; phosphamidon; fensulfothion; PennCap-M (microencapsulated methyl parathion); disulfoton; phorate; methamidophos; carbofuran; aldicarb; methomyl; and captafol. Details for treating each of the 11 pesticides are presented. No acceptable chemical detoxification was found for the remaining pesticides: ronnel; dimethoate; Dyfonate; Def; EPTC; molinate; thiram; propanil; Diphenamid; chloroxuron; simazine; cyanazine; Amitrole; paraquat; PCNB; dinoseb; chloropicrin; chlorobenzilate; endrin; D-D; dibromochloropropane (DBCP); BHC; dicamba; sodium fluoroacetate (Compound 1080); creosote; and warfarin.

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ABSTRACT

This sequel to the Handbook for Pesticide Disposal by Common Chemical Methods has examined chemical detoxification/degradation methods for 40 pesticides. The objectives for this study are the same as described in the companion: to develop practical chemical methods by which the layman can detoxify pesticides and to delineate hazards associated with the detoxification methods. The 40 pesticides were selected on the basis of their toxicological properties, their consumption, and their representation of other pesticides. Chemistry was reviewed for each through literature search and personal contacts with pesticide manufacturers and other sources. Although many of the selected pesticides are susceptible to alkaline hydrolysis, this approach is only recommended for 11 of the pesticides: monocrotophos; phosphamidon; fensulfothion; PennCap-M (microencapsulated methyl parathion); disulfoton; phorate; methamidophos; carbofuran; aldicarb; methomyl; and captafol. Details for treating each of the 11 pesticides are presented. No acceptable chemical detoxification was found for the remaining pesticides: ronnel; dimethoate; Dyfonate; Def; EPTC; molinate; thiram; propanil; Diphenamid; chloroxuron; simazine; cyanazine; Amitrole; paraquat; PCNB; dinoseb; chloropicrin; chlorobenzilate; endrin; D-D; dibromochloropropane (DBCP); BHC; dicamba; sodium fluoroacetate (Compound 1080); creosote, and warfarin.

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SUMMARY

This report is a sequel to the Handbook for Pesticide Disposal by Common Chemical Methods (1). Its objectives are the same as the earlier report: to develop chemical procedures which pesticide users could utilize for detoxifying and deactivating waste pesticides and to delineate hazards associated with the chemical methods of pesticide detoxification.

The study method was basically the same used in the earlier work (1). Forty pesticides were chosen by similar criteria. The pesticides were selected based primarily upon criteria of domestic consumption, toxicity and representative chemical classes. The selected pesticides were:

- Phosphorus-containing pesticides - monocrotophos, phosphamidon, fensulfothion, ronnel, dimethoate, disulfoton, phorate, methamidophos, Def, Dyfonate, and PennCap-M (microencapsulated methyl parathion).
- Nitrogen-containing pesticides - carbofuran, aldicarb, methomyl, EPTC, molinate, thiram, propanil, captafol, Diphenamid, chloroxuron, simazine, cyanazine, Amitrole, dinoseb, PCNB, and chloropicrin.
- Halogen-containing pesticides - chlorobenzilate, 2,4,5-T, endrin, dibromochloropropane (DBCP), D-D, BHC (lindane), and dicamba.
- Inorganic and metallorganic pesticides - arsenic acid and MSMA.
- Miscellaneous pesticides - creosote, sodium fluoroacetate (Compound 1080) and warfarin.

Information on chemical degradation and the toxicity of the degradation products was collected by literature review, and contacts with pesticide manufacturers and research groups. The collected data was evaluated to identify chemical reactions which convert the pesticides to non-toxic products. Then criteria for acceptable reactions were assessed, which included availability, safety, and cost of the reagents and equipment; reaction requirements such

as temperature control; the technical abilities needed for performance; and reaction time.

Results and conclusions of this study generally agreed with the previous study (1). Although many of the pesticides responded to alkaline hydrolysis (which included the phosphorus-containing pesticides and some nitrogen-containing and halogen-containing pesticides), alkaline hydrolysis was only recommended for 11 pesticides: monocrotophos; phosphamidon; fensulfothion; PennCap-M (microencapsulated methyl parathion); disulfoton; phorate; methamidophos; carbofuran; aldicarb; methomyl; and captafol. The hydrolytic detoxification procedure is detailed: it includes preparation of the caustic decontaminant; the quantity of decontaminant to use; directions for the decontamination (e.g., method of mixing and contact time); and method for disposal of the decontaminated waste. Also, a method for rinsing empty bottles and drums with caustic decontaminant is described. Although the s-triazenes simazine and cyanazine yield less hazardous products with alkaline hydrolysis, because of their low solubilities and other factors an acceptable decontamination procedure by chemical reaction was not possible.

No simple chemical procedure was recommended for degrading the remaining pesticides for one or more of the following reasons:

- Reaction conditions and requirements were beyond the capabilities of the layman.
- Reagents were hazardous or expensive.
- Reaction rates were unknown or too slow.
- Degradation products were unknown, were toxic, or formed toxic products in the environment.

The final recommendations for the 40 selected pesticides are summarized in Table 1.

Table 1. Chemical Disposal of the 40 Selected Pesticides

Do	Don't
Use alkaline hydrolysis:	Use chemical treatment:
Monocrotophos	Ronnel
Phosphamidon	Dimethoate
Fensulfothion	Dyfonate
PennCap-M (microencapsulated methyl parathion)	Def
Disulfoton	EPTC
Phorate	Molinate
Methamidophos	Thiram
Carbofuran	Propanil
Aldicarb	Diphenamid
Methomyl	Chloroxuron
Captafol	Cyanazine
	Simazine
	Amitrole
	Paraquat
Precautions:	PCNB
Use personal protection equipment. Follow disposal procedure closely. Dispose larger quantities in several smaller batches.	Dinoseb
	Chloropicrin
	Chlorobenzilate
	2,4,5-T
	Endrin
	D-D
	BHC (Lindane)
	DBCP
	Dicamba
	Sodium Fluoroacetate
	Creosote
	Warfarin
	Arsenic Acid
	MSMA

1. INTRODUCTION

This study, Identification and Description of Chemical Deactivation/Detoxification Methods for the Safe Disposal of Pesticides, continues work initiated in Handbook of Chemical Methods for Pesticide Disposal by Common Chemical Methods (which for facilitation of discussion will be referred to as the Handbook throughout this report) (1). Both the Handbook and this present work have been sponsored by the Office of Solid Waste of the U.S. Environmental Protection Agency. The purpose of both works was to develop information on chemical methods for safely detoxifying selected pesticides. The Handbook, which was authored by Shih and Dal Porto of TRW Systems, evaluated 20 pesticides. This present study has followed the same general format as the Handbook to evaluate an additional 40 pesticides.

The Handbook selected 20 pesticides by a process which was based, in part, on numerical prioritization values and on chemical composition of the pesticides. The selection process is discussed with greater detail in Section 2. Shih and Dal Porto then gathered information in an extensive literature search and through personal contacts. They investigated chemical methods to degrade the pesticides and sought toxicity data for the degradation products. Where chemical methods rendered the pesticide non-toxic or yielded significantly less hazardous products, they determined if an acceptable procedure could be devised for the pesticide users who possess no technical training. Shih and Dal Porto only judged alkaline hydrolysis as an acceptable method for 7 of the 20 selected pesticides: naled; diazinon; guthion; malathion; carbaryl; captan; and atrazine. The selected pesticides for which they suggest alternative disposal methods include methyl parathion, dursban, maneb, alachlor, diuron, picloram, trifluoralin, methoxychlor, 2,4-D, chlordane, amiben, and pentachlorophenol. Also, they have described handling and disposal procedures for empty pesticide containers.

This present study has modeled its general study approach after the Handbook. This report, like the Handbook, consists of four sections and extensive appendices. The introduction and pesticide selection procedure are presented in Sections 1 and 2, respectively. Section 3 describes the suggested chemical detoxification, container detoxification, and alternative disposal procedures. Section 4 summarizes conclusions and recommendations for pesticide chemistry and disposal. The Appendices A, B, C, D, E, and F discuss phosphorus-containing pesticides, nitrogen-containing pesticides, halogen-containing pesticides, inorganic and metallo-organic pesticides, miscellaneous pesticides, and pesticide containers, respectively.

2. CLASSIFICATION AND SELECTION OF PESTICIDES

This study has selected pesticides for study by a modified version of the Shih and Dal Porto method (1). A few were suggested by the Office of Solid Waste of the Environmental Protection Agency because they were considered disposal problems.

Although this study has selected a broader range of pesticide classifications than included in the Handbook, a large proportion was selected from among the organophosphate esters and carbonyl-nitrogen bond containing pesticides. Studies on chemical detoxification have recognized these classes as good candidates for deactivation by a chemical hydrolysis which appears suitable for use by people with limited technical training (1-3).

2.1 PRIORITIZATION SYSTEM FOR PESTICIDE SELECTION

This study has quantitatively ranked pesticides by a modified version of the Handbook's prioritization rating system. Shih and Dal Porto calculated Prioritization Rating (PR) values by the relationship $PR = Q \cdot r_f$ where r_f and Q were the toxicological hazard and the disposal quantity factors, respectively. However, they discussed rankings as the logarithms (log PR) within the text. To facilitate discussion this study has simplified the PR calculation: Q and r_f are taken as logarithms of the numerical ratings assigned by Shih and Dal Porto, so PR is calculated by addition:

$$PR = Q + r_f.$$

Table 2 defines the assignments of Q and r_f values. Seven hazard categories were assessed: oral, inhalation, dermal, and aquatic toxicities; teratogenicity; mutagenicity; and carcinogenicity. The PR value was calculated from the highest r_f value in any one category. When several comparable pesticides

Table 2. Prioritization Rating (PR) Factors: Q and r_f

	Q or r_f Value			
	3	2	1	0
Q				
Annual Consumption in Metric Tons (mm lbs)	>45,400 (>100)	4,540-45,400 (10-100)	454-4,540 (1-10)	<454 (<1)
r_f[a]				
1. Oral Toxicity	LD_{50} <5 mg/kg	LD_{50} 5-50 mg/kg	LD_{50} 50-500 mg/kg	LD_{50} 500-5000 mg/kg
2. Inhalation Toxicity	LC_{50} $\leq$ 50 ppm or $\leq$ 0.5 mg/l or OSHA 1 ppm	LC_{50} 50-200 ppm or 0.5-2mg/l or OSHA 1-10 ppm	LC_{50} 200-2000 ppm or OSHA 10-100 ppm	OSHA 100-1000 ppm
3. Dermal Toxicity	LD_{50} $\leq$ 20 mg/kg 24 hr. skin contact	LD_{50} 20-200 mg/kg 24 hr. skin contact	Corrosive to skin	Lachrymators
4. Aquatic Toxicity	TL_m <1 mg/l	TL_m 1-10 mg/l	TL_m 10-100 mg/l	TL_m 100-1000 mg/l
5. Teratogenicity	Known to be teratogenic			Not known to be teratogenic
6. Carcinogenicity	Known to be carcinogenic			Not known to be carcinogenic
7. Mutagenicity	Known to be mutagenic			Not known to be mutagenic

[a] r_f is the highest value of r_f exhibited by the pesticide in any hazard category.

were assigned identical PR values, the individual toxicities were evaluated for each pesticide. If further information on r_f assignment is wished, the Handbook should be consulted. The prime sources for toxicological data were the Registry of Toxic Effects of Chemical Substances (4) (referred to as the Registry) and Water Quality Criteria 1972 (5). While the latter contained aquatic toxicity data, the former is a compendium of information on the other toxicity categories. The r_f values for oral, dermal, and inhalation toxicities used, when available, values for rats as the common test organism. Where no rat data was available, either data for an alternative organism was taken and/or other sources of toxicity data were accepted. The Registry also records positive tests for carcinogenesis and teratogenesis; no positive mutagenic test was reported for any of the selected pesticides. The r_f value of 3 was assigned to pesticides with positive carcinogenic or teratogenic tests. The Registry lists feeding tests in which neoplastic effects were identified; they were also assigned r_f values of 3.

Since no quantitative data on pesticide disposal were available, Shih and Dal Porto estimated the disposal quantity factor, Q, from data on production volumes. They tacitly assumed that disposal is directly related to annual domestic production volume. Market data published in Stanford Research Institute's Chemical Economics Handbook on consumption volume would better estimate the disposal factor, Q (6). The marketing data are related by the relationship

Consumption = Production + Import - Export

Some pesticides, such as paraquat and phosphamidon (Dimecron), are not even domestically produced, but significant amounts (> 454 metric tons active ingredients) are imported annually (2, 6).

2.2 CLASSIFICATION OF PESTICIDES

Table 3 describes the pesticide classification scheme used in this study. This scheme classifies pesticides according to chemical characteristics. The Midwest Research Institute (MRI) originated this classification in their report, Guidelines for the Disposal of Small Quantities of Unused Pesticides (2). Shih and Dal Porto modified this classification scheme in the Handbook (1). They excluded inorganic pesticides and reduced the number of categories in the nitrogen-containing pesticide class and in the process grouped together pesticides of different chemical reactivity. For example, they classed together amines, nitro-compounds and quaternary ammonium compounds. The pesticide classification system used in this report was better adapted to select pesticides with a wide variety of chemical reactivity.

2.3 SELECTED PESTICIDES

The 40 selected pesticides are listed by their chemical classification in Table 4. Tables 5 and 6 summarize salient toxicological information, consumption data and calculated PR values. Table 7 reports ancillary information on environmental persistence, mobility in soil and aqueous solubility.

i) Inorganic and Metallo-organic Pesticides

Only arsenicals were selected from this classification. Overall arsenical consumption was estimated about 7.3 to 7.7 metric tons (16 to 17 million pounds); roughly two thirds were methylarsenic derivatives (6c). Monosodium methanearsonate (MSMA) which has a PR value of 3 was selected to represent the methylarsonates (which includes DSMA, CAMA, and cacodylic acid). Since it is the most highly consumed, arsenic acid (PR of 3) was also selected. It typifies the other inorganic arsenic containing pesticides (such as calcium and lead arsenate and sodium arsenite).

Table 3. Pesticide Classification System

Pesticide Classification	Typical Pesticides of Each Classification
I. Inorganic and organometallic pesticides	
1. Arsenic-containing compounds	Arsenic trioxide, DSMA, Calcium arsenate
2. Mercury-containing compounds	Phenylmercuric acetate, Mercurous chloride
3. Other inorganics and metallo-organics	DuTer (Triphenyl tin), Ammate, Copper, Sodium chlorate
II. Phosphorus-containing pesticides	
1. Phosphates and phosphonates	Ciodrin, Dicrotophos, Monocrotophos, Dichlorvos, Phosphamidon, TEPP
2. Phosphorothioates and phosphonothioates	Abate, EPN, Fensulfothion, Fenthion, Parathion, Ronnel
3. Phosphorodithioates and phosphonodithioates	Carbophenathion, Dimethoate, Disulfoton, Dyfonate, Phorate
4. Phosphorus-nitrogen compounds	Crufomate, Monitor
5. Other phosphorus-containing pesticides	DEF, Folex
III. Nitrogen-containing pesticides	
1. Carbamates and related compounds	Carbaryl, Aldicarb, Baygon, BuxTen, Carbofuran, Metacil, Methomyl
2. Thiocarbamates	Diallate, EPTC, Mollinate, Pebulate
3. Dithiocarbamates	Amobam, Mancozeb, Polyram, Vapam
4. Anilides	CDAA, Propachlor, Propanil
5. Imides and Hydrazides	Folpet, Maleic hydrazide, Norbormide
6. Amides	Devrinol, Diphenamid
7. Ureas and Uracils	Chloroxuron, Diuron, Linuron, Monuron
8. Triazenes	Bladex, Pramitol, Simazine
9. Heterocyclic amines	Amitrol, DMTT, Mylone
10. Nitro-compounds	Benefin, Dinoseb, PCNB
11. Quaternary ammonium compounds	Diquat, Paraquat
12. Other Nitrogen-containing compounds	Antu, Chloropicrin, Dodine

Table 3. (Cont'd.)

Pesticide Classification	Typical Pesticides of Each Classification
IV. Halogen-containing pesticides	
1. DDT related compounds	Chlorobenzilate, Kelthane, Perthane
2. Chlorophenory compounds	2,4-D,2,4,5,T, Erbon, Silvex
3. Aldrin-Toxaphene group	Aldrin, Dieldrin, Heptachlor, Kepone, Toxaphene
4. Aliphatic and alicyclic chlorinated compounds	BHC, Carbon tetrachloride, D-D, Ethylene dichloride, Lindane
5. Aliphatic brominated compounds	Dibromochloropropane, Ethylene dibromide, Methyl bromide
6. Dihaloaromatic compounds	Dicamba, Dichlorobenzene
7. Highly halogenated aromatic compounds	Dacthal, Pentachlorophenol, Tetrachlorophenol
V. Miscellaneous pesticides	
1. Sulfur containing pesticides	Omite, Dexon, Sulfoxide
2. Botanical and Microbiological pesticides	Rotenone, Strychnine, Pyrethrin
3. Organic pesticides, not elsewhere enumerated	Acrolein, Carbon disulfide, Creosote, Endothal, Warfarin, Sodium fluoroacetate

Table 4. List of Selected Pesticides

Pesticide Class	Selected Pesticides
1. Phosphorus-Containing Pesticides	
Phosphates and Phosphonates	Monocrotophos, Phosphamidon
Phosphorothioates and Phosphonothioates	Fensulfothion, Ronnel, PennCap-M (microencapsulated methyl parathion)
Phosphorodithioates and Phosphonodithioates	Dimethoate, Disulfoton, Dyfonate, Phorate
Phosphorus-Nitrogen Compounds	Methamidophos
Other Phosphorus-Containing Pesticides	Def
2. Nitrogen-Containing Pesticides	
Carbamates	Carbofuran, Aldicarb, Methomyl
Thiocarbamates	EPTC, Molinate
Dithiocarbamates	Thiram
Anilides	Propanil
Imides and Hydrazides	Captafol
Amides	Diphenamide
Ureas and Uracils	Chloroxuron
Triazenes	Cyanazine, Simazine
Heterocyclic Amines	Amitrole
Quaternary Ammonium Compounds	Paraquat
Aromatic Nitro Compounds	PCNB, Dinoseb
3. Halogen-Containing Pesticides	
DDT Related Compounds	Chlorobenzilate
Chlorophenoxy Compounds	2,4,5-T
Aldrin-Toxaphene Group	Endrin
Aliphatic and Alicyclic Chlorinated Compounds	D-D, BHC (Lindane)
Aliphatic Brominated Compounds	DBCP
Dihalogenated Compounds	Dicamba
4. Inorganic and Organometallic Pesticides	
	Arsenic Acid, MSMA
5. Miscellaneous Pesticides	
	Sodium fluoroacetate, Creosote, Warfarin

Table 5. Consumption Volume and Hazard Properties of the Selected Pesticides. Part 1. Consumption Volume

Pesticide	Annual Consumption$^{\Delta}$ MM Pounds	 Metric Tons	Production Rating, Q
MSMA	9.4	4262.9	1
Arsenic acid	6.0	2721.0	1
Monocrotophos	4.2	1904.7	1
Phosphamidon	1.5	680.3	1
Fensulfothion	4.2	1904.7	1
Ronnel	1.1	498.9	1
PennCap-M	--	--	-
Dimethoate	2.3	1043.1	1
Disulfotan	5.6	2539.6	1
Dyfonate	3.6	1632.6	1
Phorate	7.7	3492.0	1
Monitor	0.8	362.8	0
Def	6.5	2947.8	1
Aldicarb	2.7	1224.5	1
Carbofuran	13.4	6076.9	1
Methomyl	5.3	2403.6	1
Eptam (EPTC)	6.4	2902.4	1
Molinate	2.7	1224.5	1
Thiram	0.7	317.5	0
Propanil	9.0	4081.5	1
Captafol	4.0	1814.0	1
Diphenamid	2.5	1133.8	1
Chloroxuron	1.0	453.5	1
Bladex	7.3	3310.6	1
Simazine	7.8	3537.3	1
Amitrole	1.4	634.9	1
Dinoseb	6.2	2811.7	1
Pentachloronitrobenzene (PCNB)	2.3	1043.1	1

Table 5. Consumption Volume and Hazard Properties of the Selected Pesticides. Part 1. Consumption Volume (Cont'd.)

Pesticide	Annual Consumption^Δ MM Pounds	Annual Consumption^Δ Metric Tons	Production Rating, Q
Paraquat	1.6	725.6	1
Chloropicrin	7.8	3537.3	1
Chlorobenzilate	1.0	453.5	1
2,4,5-T	6.7	3038.5	1
Endrin	1.2	544.2	1
Benzene hexachloride (BHC)	1.0	453.5	1
D-D	56.5	25,622.8	2
Dibromochloropropane (DBCP)	22.4	10,158.4	2
Dicamba	2.8	1269.8	1
Creosote	1000.	453,500.	3
Warfarin	12	5422.0	2
Sodium fluoroacetate	<1	<453.5	0

Δ Reference 6

Table 6. Consumption Volume and Hazard Properties of the Selected Pesticides. Part 2. Hazard Properties and Ratings.

Pesticide	Acute Oral LD_{50} [a*] (mg/kg)	Acute Dermal LD_{50} [a*] (mg/kg)	Inhalation Toxicity[a*] (ppm)	Aquatic Toxicity** LC_{50} (mg/ℓ)	Other Hazards[a] *	Hazard Rating (r_f)	Priority Ranking Value (r_f + Q)
MSMA	50[b]					2	3
Arsenic acid	48					2	3
Monocrotophos	21	112				2	3
Phosphamidon	17	125		4.5-100 (96 hrs)[k]		3	4
Fensulfothion	2	3				3	4
Ronnel	906	2000		0.305 (96 hrs)[k]		3	4
PennCap-M	>60	1200[f]					
(Methyl Parathion)	(9)	(67)					
Dimethoate	147, 30[c]	353		<1 (96 hrs)[k]		3	4
Disulfotan	2[d], 3.2[e]	6		0.063-3.7 (96 hrs)[k]		3	4
Dyfonate	3	147				3	4
Phorate	1	3		0.0006 (96 hrs)[l]		3	4
Monitor	7.5	118[f]				2	2
Def	150	168		0.1 (96 hrs)[l]		3	4
Aldicarb	1.0	1400[f]				3	4
Carbofuran	11[c], 5.3	1100[c], 120	8.5 mg/cu m			3	4
Methomyl	17	1500				2	3
EPTC	112[g], 1630	1460[f]	200 mg/cu m (3 hrs)[d]	2.3 (96 hrs)[l]		2	3
Molinate	501	>2000		0.3-4.5 (96 hrs)[l]		3	4
Thiram	560				Teratogenic[h]	3	3
Propanil	560			16.0 (96 hrs)[l]		1	2
Captafol	2500			0.8 (96 hrs)[l]	Teratogenic[i]	3	4
Diphenamid	293			50-58 (48 hrs)[l]		1	2
Chloroxuron	10[j], 3700	10,000		25 (48 hrs)[k]		2	3
Cyanazine	340					1	2
Simazine	5000			6.6 (48 hrs)[k]		1	2
Amitrol	1100			3.0-3.2 (48 hrs)[l]	Carcinogenic[h]	3	4
Dinoseb	25	80			Teratogenic[h]	3	4
PCNB	1650				Carcinogenic[h]	3	4
Paraquat	57	80		3.7-11 (48 hrs)[l]	Teratogenic	3	4
Chloropicrin	250		2400 mg/cu m/M[c,d]			3	4
Chlorobenzilate	700		500 ppm[b]		Carcinogenic[h]	3	4
2,4,5-T	300				Teratogenic	3	4

Table 6. Consumption Volume and Hazard Properties of the Selected Pesticides. Part 2. Hazard Properties and Ratings (Cont'd).

Pesticide	Acute Oral LD_{50} ^{a*} (mg/kg)	Acute Dermal LD_{50} ^{a*} (mg/kg)	Inhalation Toxicity^{a*} (ppm)	Aquatic Toxicity** LC_{50} (mg/ℓ)	Other Hazards^{a*}	Hazard Rating (r_f)	Priority Ranking Value (r_f + Q)
Endrin	3	15		0.0005-0.0012 (96 hrs)^{k}		3	4
BHC	88,840$^{c, d}$				Carcinogenic^{h}	3	4
D-D	140	2100^{f}	1000 ppm (4 hrs)			1	3
DBCP	173	1400^{f}	103 ppm (8 hrs)		Carcinogenic	2	4
Dicamba	1040			20.0 (96 hrs)		1	2
Creosote	600$^{d, g}$					0	3
Warfarin	3-200^{j}					3	5
Sodium fluoro-acetate	0.22	20^{f}	300 mg/cu m (10 min)		Teratogenic^{m}	3	3

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* Reference 4

** Reference 5

- See Appendices A-G for references

(a) For rats unless otherwise specified
(b) Unknown mammal
(c) Human
(d) LD_{Lo} or LC_{Lo}
(e) Wild Bird
(f) Rabbit
(g) Cat
(h) Mouse
(i) Hamster
(j) Dog
(k) Fish
(l) Crayfish
(m) Warfarin sodium

Table 7. Soil Persistence, Soil Mobility and Water Solubility of the Selected Pesticides.

Pesticide	Soil[+] Persistence (months)	Mobility[+]	Water Solubility[‡]
MSMA			soluble
Arsenic acid			167 g/ℓ
Monocrotophos			miscible
Phosphamidon			miscible
Fensulfothion			1.6 g/ℓ
Ronnel			44 ppm
PennCap-M (Methyl Parathion)			55-60 ppm
Dimethoate			25-39 g/ℓ
Disulfotan			25 ppm
Dyfonate			13 ppm
Phorate	1-3	slightly mobile	50 ppm
Monitor			90 g/ℓ
Def			insoluble
Aldicarb			6 g/ℓ
Carbofuran			700 ppm
Methomyl			58/ℓ
EPTC	1-3	slightly mobile	365 ppm
Molinate			800 ppm
Thiram			30 ppm
Propanil			225 ppm
Captafol			1.4 ppm
Diphenamid			260 ppm
Chloroxuron			3.7 ppm
Cyanazine			171 ppm
Simazine	3-12	slightly mobile	5 ppm
Amitrol			280 g/ℓ
Dinoseb			50 ppm
PCNB			0.44 ppm
Paraquat			soluble
Chloropicrin			2.3 g/ℓ
Chlorobenzilate			insoluble
2,4,5-T	3-12	mobile	278 ppm (free-acid) soluble (amine salts)
Endrin	>12	immobile	insoluble
BHC	>12		0.5-1.0 ppm
D-D			2 g/ℓ
DBCP			1 g/ℓ
Dicamba			4.5 g/ℓ
Creosote			very slightly soluble
Warfarin			40 ppm (free acid) soluble (Warfarin sodium)
Sodium fluoroacetate			very soluble

[+] Reference 2

[‡] See Appendices A-G for references.

Other inorganic pesticides were eliminated either for reasons of low consumption or no problem in disposal. Mercurials (inorganic and organic) have a high environmental hazard but relatively low consumption. Although 0.9 to 1.4 metric tons (2 to 3 million pounds) were consumed, most was used in wood preservatives or in paints (6c). Inorganic pesticides with high consumption but no apparent disposal problem include sulfur, copper salts, sodium chlorate, and ammate.

ii) Phosphorus-Containing Pesticides

a. Phosphates and Phosphonates

Phosphamidon was chosen since it had the highest PR value of 4. Monocrotophos and ciodrin have PR values of 3. Both are phosphate esters of (ε)-3-hydroxycrotonamide; they differ only by the amide substituent. Monocrotophos was selected because of higher consumption and greater oral toxicity. Dichlorovos (PR = 4) was not chosen since it can be degraded by the same procedure recommended for naled in the Handbook (1).

b. Phosphorothioates and Phosphonothioates

PennCap-M, a microencapsulated formulation of methyl parathion, was selected. Although Shih and Dal Porto reviewed methyl parathion disposal in the Handbook, information on the effect of microencapsulation on product disposal was desired. Fensulfothion and ronnel (Korlan) were selected since their PR values were 4.

c. Phosphorodithioates and Phosphonodithioates

Dimethoate, disulfoton, Dyfonate and phorate all received PR values of 4. Since the four were judged good candidates for chemical deactivation (2, 3) they were all selected. Before chemical deactivation could be recommended, the conditions of the chemical reactions had to be assessed, and degradation products identified and their toxicities evaluated.

d. Phosphorus-Nitrogen Compounds

Methamidophos (Monitor) and cruformate both had PR values of 2. Monitor was chosen since its hazard rating was higher. Both pesticides had similar consumption volumes. While Monitor was slightly below Q-value cutoff (363 metric tons), cruformate was slightly above (454 metric tons).

e. Other Phosphorus-Containing Pesticides

Def, a phosphorotrithioate, pesticide, was assigned a PR value of 4. It was selected for study.

iii) Nitrogen-Containing Pesticides

a. Carbofuran (PR value of 5) and aldicarb (PR value of 4) were selected since they had the highest PR values of the carbamates. Since the carbamates are known to be susceptible to chemical degradation, another carbamate, methomyl, was also selected. It was chosen over several other candidates with PR values of 3 (Baygon, Buxten, chloropropham and metacil), because it was consumed in significantly greater quantity.

b. Thiocarbamates

Molinate and EPTC (Eptam) were selected. Molinate received a PR value of 4. EPTC and diallate both were assigned PR values of 3. EPTC was chosen since its consumption is greater than ten times that of diallate.

c. Dithiocarbamates

Several dithiocarbamates have displayed teratogenic effects in feeding studies with rodents (4). Although the ethylene bisdithiocarbamate pesticides are consumed in greater quantities than any other dithiocarbamates

(6), they were not considered useful for study. Shih and Dal Porto reviewed chemistry for maneb, which will possess chemical reactivity characteristic of all ethylene bisdithiocarbamates. Thiram was selected as a representative for this study since it was consumed in larger amounts than other candidate dithiocarbamates (including CDEC and ziram).

d. Anilides

Propanil and propachlor both received PR values of 2. Although the annual consumption for the two were similar (4,938 and 4,082 metric tons for propachlor and propanil, respectively) (6), they were assigned different Q values. Propachlor was slightly above cutoff, so it fell into the Q-value 2 range. Propanil was selected for study because it has a higher hazard rating.

e. Imides and Hydrazides

Three pesticides (maleic hydrazide, captafol, and folpet) received PR values of 4. Captafol was selected since its known consumption was highest (1814 metric tons). Folpet consumption, in comparison, was only 816 metric tons for the same year, 1974 (6). The SRI report did not list maleic hydrazide consumption, since it is a plant growth regulator. The MRI study estimated 1971 production at 1361 metric tons (2).

f. Amides

A PR value of 2 was given to diphenamide. Since this was the highest PR value of the group, it was selected.

g. Ureas and Uracils

Chloroxuron and monuron were assigned PR values of 3. Chloroxuron was selected since its consumption was greater (454 versus 91 metric tons).

h. Triazines

Shih and Dal Porto suggest that the triazines have good potential for chemical degradation (1). Cyanazine (Bladex) and simazine both were chosen since they are consumed in moderate quantities (approximately 3,300-3,500 metric tons for 1974). Cyanazine has a relatively high oral toxicity (LD_{50} of 340 for rats) among triazene herbicides. Simazine's hazard results from its moderate aquatic toxicity.

i. Heterocyclic Amines

Amitrole was the only member of this class selected. It was assigned a PR value of 3.

j. Nitro-Compounds

PCNB (Terrachlor) which had the highest PR value (of 4) for this group was selected. Dinoseb and benefin were assigned PR values of 3. Dinoseb was selected since it was consumed by almost five-fold more than benefin in 1974 (6c).

k. Quaternary Ammonium Compounds

Paraquat was assigned the highest PR value, 5. The only other QAC with a moderate PR value was diquat, which received a value of 3. However, its consumption was less than 100 metric tons in 1974.

l. Other Nitrogen-Containing Compounds

Chloropicrin was selected because of its PR value of 4.

iv) Halogen-Containing Pesticides

a. DDT-related Pesticides

Chlorobenzilate which received a PR value of 4 was the only DDT analog chosen, since it was the highest of this class. Kelthane was assigned a PR value of 3.

b. Chlorophenoxy Compounds

Both 2,4,5-T and silvex were assigned PR values of 4. 2,4,5-T was selected because of higher consumption (3039 *versus* 907 metric tons).

c. Aldrin-Toxaphene Group

Aldrin, dieldrin, endrin, endosulfan, and heptachlor were all issued PR values of 4. Since they are expected to behave more or less similarly in chemical treatments, endrin was chosen as the representative (2).

d. Aliphatic and Alicyclic Chlorinated Hydrocarbons

Dichloropropene-dichloropropane (D-D) and carbon tetrachloride both received PR values of 5. Both are fumigants which are liquid at room temperature. D-D was selected. Carbon tetrachloride was not chosen, since it is primarily an industrial chemical. Benzene hexachloride (BHC) and ethylene dichloride were assigned PR values of 4. BHC was selected for study. Ethylene dichloride was not selected since two other chlorinated hydrocarbons and one brominated hydrocarbon, DBCP, were selected and they are expected to behave similarly.

e. Aliphatic Brominated Compounds

Dibromochloropropane (DBCP) and methyl bromide were given PR values of 4. Methyl bromide is a gas at ambient temperatures and usually handled in returnable containers (1). DBCP was selected. It is a liquid at ambient temperature. Also, recent evidence has demonstrated that it causes sterility in human males (7).

f. Dehaloaromatic Compounds

Although dichlorobenzene was assigned a PR value of 5 it was not selected for study. Its hazard rating of 3 results from a positive test for carcinogenesis (4). It is heavily used (27,216 metric tons) as a fumigant, mostly as the familiar household mothballs. It is not considered a disposal problem (1). Dicamba, with a PR value of 3 was selected for study.

g. Highly Halogenated Aromatic Compounds

No pesticide of this class was selected since its members (for example, tetrachloro- and trichlorophenol) are similar to pentachlorophenol. Pentachlorophenol was evaluated in the Handbook (1).

v) Other Pesticides

Included in this class are sulfur-containing pesticides, botanical and microbiological pesticides, and "organic pesticides not elsewhere enumerated." Since the highest PR value for a sulfur-containing pesticides was 1, none were selected for study. Rotenone and strychnine both were given PR values of 3. Since their consumption is minor and they do not characterize other pesticides, they were not included for study. Among the "organic pesticides not included elsewhere" PR values were assigned as 5 for warfarin, 4 for carbon disulfide, and 3 for sodium fluoroacetate, creosote, and endothal. Since carbon disulfide is primarily an organic reagent, it was not selected. Sodium fluoroacetate and creosote were selected since their disposal are now of interest to EPA. Warfarin was selected since it has a high PR value and the sodium salt, warfarin sodium, gave a positive test for teratogenicity (4).

3. CHEMICAL METHODS FOR THE DISPOSAL OF SELECTED PESTICIDES

Chemical methods to detoxify or deactivate the 40 selected pesticides were reviewed and evaluated by similar procedures to those used in the companion study, Handbook for Pesticide Disposal by Chemical Methods (1). This has included literature search and personal contact with pesticide manufacturers and formulators and with research workers. The results and conclusions of the review are summarized in Appendices A through E for the phosphorus-containing, nitrogen-containing, halogen-containing, inorganic and organometallic, and "miscellaneous" pesticides, respectively. Also, a review of recent literature on the effectiveness of container rinsing for removing residues from empty containers is presented in Appendix F.

Conclusions of the present study generally agree with the companion report (1). Alkali in aqueous solution or aqueous ethanol solution was suggested for decontaminating 11 pesticides: monocrotophos; phosphamidon; fensulfothion; disulfoton; phorate; methamidophos; PennCap-M (microencapsulated methyl parathion); carbofuran; aldicarb; methomyl; and captafol. Alkaline solution is recognized as a relatively hazardous material, but other caustic products, such as household oven cleaners, have comparable hazards.

This study recommends the same general approach to alkaline hydrolysis as the Shih and Dal Porto report (1). Table 8 describes personal protection equipment for alkaline decontamination. Table 9 summarizes the conditions for decontamination of the selected pesticides. It includes decontaminant solution composition, the amount of decontaminant to use, and the contact time for each pesticide. The contact times were estimated from the time calculated for 99.9%

Table 8. Personal Protection Equipment For Pesticide Disposal. Adapted from Shih and Dal Porto (1).

The decontaminant solution recommended for the chemical detoxification of pesticides and pesticide containers in most cases is strong caustic that can severely burn skin, eyes, or any body tissue. In addition, inhalation and skin contact with the pesticides is extremely dangerous. To avoid contact with the decontaminant solution and the pesticide in the disposal of small quantities of pesticides or pesticide containers, the following protective equipment is recommended:

1. Impervious or rubber head covering.
2. Protective eye goggles.
3. Organic vapor respirators, cartridge type.
4. Washable work clothing.
5. Natural rubber gloves.
6. Latex rubber apron, ankle length.
7. Rubber work shoes or overshoes.

It should be noted that most household gloves deteriorate when handling organophosphates and therefore should not be used. Also, leather shoes should not be worn. The organic vapor respirators could be any type approved by the U.S. Department of Agriculture.

The rubber gloves, shoes, apron, and head covering may be obtained through a rubber goods house or safety equipment companies. The eye goggles, work clothing and organic vapor respirator may be obtained from safety equipment companies or sometimes through the Sears and Roebuck farm catalog.

Table 9. Recommended Decontaminant Solution and Contact Time for the Chemical Detoxification of Selected Pesticides.

Pesticide	Formulation[a]	Decontaminant Solution	Ratio of Decontaminant Solution to Formulation	Contact Time
Monocrotophos (Azodrin)	3.2 lb/gal WM	10% NaOH	4:1 by volume	12 hours (overnight)
	4.0 lb/gal WM	10% NaOH	5:1 by volume	12 hours (overnight)
	80% WP	10% NaOH	1 gal/lb	12 hours (overnight)
Phosphamidon (Dimecron)	8 lb/gal WM	10% NaOH	8:1 by volume	1 hour
	10 lb/gal WM	10% NaOH	10:1 by volume	1 hour
Fensulfothion (Dasanit)	6 lb/gal SC	5% NaOH in 50% Aqueous Ethanol	12:1 by volume	4 hours
		or 10% NaOH in 50% Aqueous Ethanol	6:1 by volume	2 hours
	15% Granular	5% NaOH in 50% Aqueous Ethanol	1 quart/lb	12 hours (overnight)
	10% Granular	5% NaOH in 50% Aqueous Ethanol	1 quart/lb	12 hours (overnight)
	10% Dust	5% NaOH in 50% Aqueous Ethanol	1 quart/lb	12 hours (overnight)
Disulfoton (Di-Syston)	10% Granular	5% NaOH in 50% Aqueous Ethanol	2 quarts/lb	3 hours
	50% Granular	5% NaOH in 50% Aqueous Ethanol	1 quart/lb	3 hours
	2% Granular	5% NaOH in 50% Aqueous Ethanol	1 quart/lb	3 hours

Table 9. Recommended Decontaminant Solution and Contact Time for the Chemical Detoxification of Selected Pesticides (Cont'd).

Pesticide	Formulation[a]	Decontaminant Solution	Ratio of Decontaminant Solution to Formulation	Contact Time
Phorate (Thimet)	6 lb/gal EC	10% NaOH in 50% Aqueous Ethanol	6:1 by volume	15 minutes
Methamidophos (Monitor)	4 lb/gal	10% NaOH	8:1 by volume	15 minutes
PennCap-M (microencapsulated methyl parathion)	2 lb/gal	5% NaOH in 50% Aqueous Ethanol	8:1 by volume	12 hours (overnight)
Carbofuran (Furadan)	4 lb/gal F	10% NaOH in 50% Aqueous Ethanol	10:1 by volume	30 minutes
	10% Granular	5% NaOH in 50% Aqueous Ethanol	2 quarts/lb	2 hours
Aldicarb (Temik)	15% Granular	10% NaOH in 50% Aqueous Ethanol	1 gal/lb	12 hours (overnight)
	5% or 10% Granular	10% NaOH in 50% Aqueous Ethanol	2 quarts/lb	12 hours (overnight)
Methomyl (Lannate, Nudrin)	1.8 lb/gal F	10% NaOH	5:1 by volume	3 hours
	90% water sol. dust	10% NaOH	1 gal/lb	12 hours (overnight)
	2, 5% dust	10% NaOH	1 quart/lb	12 hours (overnight)

Table 9. Recommended Decontaminant Solution and Contact Time for the Chemical Detoxification of Selected Pesticides (Cont'd).

Pesticide	Formulation[a]	Decontaminant Solution	Ratio of Decontaminant Solution to Formulation	Contact Time
Captafol	4 lb/gal F	10% NaOH in 50% Aqueous Ethanol	10:1 by volume	15 minutes
	80% WP	10% NaOH in 50% Aqueous Ethanol	1 gal/lb	1 hour

EC - Emulsifiable
F - Flowable
SC - Spray Concentrate
WM - Water Miscible
WP - Wettable Powder

pesticide degradation. Additional time was added as safety margins to approximate the time for mixing, dissolution, and desorption of active ingredients from dusts, powders, and granules, and other unknown factors. The discussion in the Appendices has used alkaline normality for calculating degradation times. The concentrations of 5% and 10% sodium hydroxide are slightly higher than 1 and 2N, respectively. Table 10 summarizes the decontamination procedures suggested for use with the recommendations of Table 9.

The pesticides not detoxified by chemical treatment must be disposed by an acceptable alternative. The EPA has published recommended procedures for pesticide disposal and storage (40 CFR 165) and criteria for solid waste disposal facilities (40 CFR 257) (7a, 7b). Since recommendations for alternative disposal procedures are beyond the scope of this present report, the regional EPA or appropriate state authorities should be contacted for specific information on acceptable, alternative disposal procedures.

Empty pesticide containers should also be disposed safely. The Environmental Protection Agency has recommended specific procedures (7a). If possible, containers should be triple rinsed using the procedure outlined in Table 11.

An alkaline rinse solution is recommended when pesticide residues can be detoxified by hydrolysis. If the pesticide is not water soluble, the aqueous alkali might not be effective. Aqueous ethanolic caustic more effectively detoxifies these pesticides (Appendix F). Pesticides which can use aqueous caustic are monocrotophos, phorate, phosphamidon, methamidophos, and methomyl. Pesticides which should use the aqueous-ethanolic caustic are fensulfothion, disulfoton, PennCap-M (encapsulated methyl parathion), carbofuran, aldicarb, and captafol. Table 12 describes the recommended procedure for the caustic rinse.

Table 10. Pesticide Disposal Procedure - Chemical Detoxification by Alkali Treatment. Adapted from Shih and Dal Porto (1).

This procedure is only applicable to the present study. Do not use this procedure for other pesticides since decomposition products are unknown and may be harmful. The quantity of decontaminant solution to be used is given in Table 9. Note that caustic soda (lye) absorbs moisture and should be stored in a tightened container. The disposal procedure is outlined as follows:

1. Use personal protection equipment (Table 8).

2. Carefully mix water, ethanol (if recommended) and caustic soda (lye) in a container to make up the recommended decontaminant solution (Table 9). Note that the reaction between caustic soda and water generates heat and splattering may occur. To make up 1 gal of the 5% NaOH - 50% ethanol solution, use 1 cup of caustic soda with 2 qts of ethanol and 1-3/4 qts of water. To make up 1 gal of the 10% NaOH solution, use 2 cups of caustic soda with 3-1/2 qts of water. To make up 1 gal of the 10% NaOH - 50% ethanol solution use 2 cups of caustic soda, 2 qts of ethanol and 1-3/4 qts of water. Allow the solution to cool before any use.

3. Place pesticide requiring disposal in a 5 gal metal container. The container should be one that has been used for the same type of pesticide or one that has not been previously used for pesticides and other chemicals. Add the recommended amount of decontaminant solution (Table 9) to the pesticide. Do not fill up more than half of the container. Larger quantities of pesticides should be disposed of in several smaller batches.

4. Tighten the bungs and other closures. Rotate the container carefully to promote the mixing between the pesticide formulation and decontaminant solution.

5. Let the container and reaction mixture stand for at least 15 minutes with occasional agitation. Consult Table 9 for the recommended contact time for each pesticide formulation.

6. Carefully loosen closures to vent any pressure build-up. Remove all bungs and closures and drain the reaction product mixture into a pit or trench at least 18 inches deep, located in non-crop land away from water supplies. Cover with earth.

7. Flush inside and outside of container with clear water.

8. Tighten all bungs and closures. Puncture the container with a pick axe or chisel and crush immediately and recycle for scrap to a steel melting plant. If container recycle cannot be accomplished, bury the container at least 18 inches deep in an isolated area away from water supplies or at an approved dump site.

Table 11. NACA Triple Rinse and Drain Procedure.
From Shih and Dal Porto (1).

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1. Empty container into spray tank. Then drain in vertical position for 30 seconds.

2. Add a measured amount of rinse water (or designated spray carrier) so container is 1/4 to 1/5 full. For container size less than 1 gallon, add an amount of rinse solution equal to 1/4 of the container volume. For a 1 gallon container, add 1 quart of rinse solution. For a 5 gallon container, add 1 gallon of rinse solution. For 30 and 55 gallon containers, add 5 gallons of rinse solution.

3. Replace closure. Shake container or roll and tumble to get rinse on all interior surfaces. Drain rinse solution into sprayer or mix tank. Continue draining for 30 seconds after drops start.

4. Repeat the above steps for total of 3 rinses. One gallon and 5 gallon steel containers should be punctured before draining the 3rd rinse. It is recommended that the container be punctured in the top near the front sprout to allow for complete drainage of the third rinse.

5. For 30 and 55 gallon steel containers, replace closures and secure tightly and send the containers to an approved drum reconditioner (check with State Department of Agriculture for list) or recycle as scrap into a steel melting plant. For 1 gallon and 5 gallon steel containers, crush immediately and recycle for scrap to a steel melting plant. For glass containers, break or crush into large container (such as 55 gallon open headed drum with cover) and recycle for scrap to a glass melting plant. If the above preferred container disposal method cannot be accomplished, the container should be crushed and buried at an approved dump site. Do not reuse containers.

Table 12. Pesticide Container Decontamination Procedure With Caustic Soda. Adapted from Shih and Dal Porto (1)

This procedure is only applicable to empty glass and metal containers. Do not use this procedure for containers of other pesticides without consulting the pesticide manufacturer or EPA personnel. The procedure is outlined as follows:

1. Use personal protection equipment (Table 8).

2. Drain container as completely as possible to spray tank or to another container for chemical detoxification. In the latter case, do not mix the pesticide with other types of pesticide formulations. Follow the pesticide detoxification procedure described in Table 10.

3. Carefully add water (or 50% aqueous ethanol), detergent and caustic soda (lye) and tighten the bungs and other closures. The amount of rinse solution to be added depends on the container size.

Container Size	Water	Detergent	Caustic Soda (Lye)
Less than 5-gallon	1 pint	1 tablespoon	--
5-gallon	2 quarts	2 tablespoons	1/2 cup
15-gallon	1-1/2 gallons	1/4 cup	1/2 pound
30-gallon	3 gallons	1/2 cup	1 pound
55-gallon	5 gallons	1 cup	2 pounds

4. Rotate the container carefully to wet all inner surfaces with the rinse solution.

5. Let the container stand 15 minutes with occasional agitation.

6. Remove all bungs and closures and bury the rinse solution at least 18 inches deep in an isolated area away from water supplies.

7. Flush inside and outside of container with clear water.

8. For 30 and 55 gal steel containers, replace closures and secure tightly and send the containers to an approved drum reconditioner (check with State Department of Agriculture for list) or recycle as scrap into a steel melting plant. For 1 gal and 5 gal steel containers, puncture with a pick axe or chisel and crush immediately and recycle for scrap to a steel melting plant. For glass containers break or crush into large container (such as 55 gal open headed drum with cover) and recycle for scrap to a glass melting plant. If container recycle cannot be accomplished, the container should be crushed and buried at least 18 inches deep in an isolated area away from water supplies or at an approved dump site. Do not reuse container.

After the container has received an appropriate rinse, large containers (30 and 55 gallon drums) could be turned over to a drum reconditioner. Rinsed, smaller containers can be land disposed as sanitary wastes. For information on the disposal of all containers which cannot be rinsed, the regional EPA office or the appropriate state authority should be contacted.

The container rinsate must also be disposed in a safe manner. According to the EPA recommended procedures (7a), the rinsate should be used as a diluent for preparing spray mixtures wherever possible. If the rinsate cannot be used for dilution and cannot be chemically detoxified/deactivated, then its disposal must follow a procedure acceptable for the pesticide active ingredient. The EPA regional office or the appropriate state authority should be contacted for further information.

4. CONCLUSIONS AND RECOMMENDATIONS

Chemical methods for detoxification and deactivation have been evaluated for 40 pesticides. This study follows an EPA-sponsored companion work on chemical detoxification methods for 20 pesticides (1). The study methods are the same and conclusions are similar. Hydrolysis with alkaline decontaminant solution is judged a practical method for detoxifying 11 pesticides of the selected pesticides: monocrotophos; phosphamidon; fensulfothion; disulfoton; phorate; methamidophos; PennCap-M (microencapsulated methyl parathion); carbofuran; aldicarb; methomyl; and captafol. Conditions for disposal of waste pesticides and empty pesticide containers is discussed in Section 3. Table 13 summarizes the salient information on chemistry and the properties of the hydrolysis products for these 11 pesticides.

Table 14 summarizes salient information on chemical reactivity and products for the pesticides which have no suitable chemical detoxification: ronnel; dimethoate; Dyfonate; Def; EPTC; molinate; thiram; propanil; Diphenamid; chloroxuron; simazine; cyanazine; Amitrole; paraquat; PCNB; DNBP; chloropicrin; chlorobenzilate; 2,4,5-T; endrin; DBCP; D-D; BHC; dicamba; MSMA; arsenic acid; sodium fluoroacetate; creosote; and warfarin. In general, one or more of the following reasons were cited for rejected chemical treatment:

- Chemical degradation products are hazardous or suspected as hazardous.
- Chemical degradation products are not known.
- Chemical reagents are expensive or hazardous.
- Chemical degradation requires advanced technical skills.
- Time required for complete degradation is too long or unknown.

Table 13. Summary of Effects of Chemical Treatment on Pesticides for which Alkali Treatment is Recommended.

Pesticide	Chemical Treatment	Degree of Degradation	Identity and Environmental Hazard of Degradation Products
Monocrotophos (Azodrin)	Alkaline hydrolysis	Complete degradation	Alkaline salts of dimethylphosphate, acetone, methylamine, and carbon dioxide are non-toxic.
	Sodium iodide	Unknown degradation rate	Desmethylmonocrotophos toxicity is unknown, but it is not an acetylcholinesterase inhibitor. Methyl iodide is slightly toxic.
Phosphamidon (Dimecron)	Acid hydrolysis	Complete degradation	Initial products are dimethylphosphate and N,N-diethyl α-chloroacetamide. The amide subsequently hydrolyzes to dimethylamine, chloroacetone, and carbon dioxide. All final and intermediate products are non-toxic.
	Sodium iodide	Unknown degradation rate	Desmethylphosphamidon toxicity is unknown, but it is not an acetylcholinesterase inhibitor. Methyl iodide is slightly toxic.
	Alkaline hydrolysis	Complete degradation	Initial products are alkaline salts of dimethylphosphate, chloride, and N,N-diethyl α-hydroxyacetamide. The amide subsequently hydrolyzes to the diethylamide of glycolic acid and alkaline acetate salts. All final and intermediate products are non-toxic.
Fensulfothion (Dasanit)	Chemical oxidation	Complete degradation	The corresponding sulfone is as toxic.
	Alkaline hydrolysis	Complete degradation	Alkaline salts of dimethylphosphate and *p*-(methylsulfamoyl) phenol are non-toxic.

Table 13. Summary of Effects of Chemical Treatment on Pesticides for which Alkali Treatment is Recommended (Cont'd).

Pesticide	Chemical Treatment	Degree of Degradation	Identity and Environmental Hazard of Degradation Products
Methamidophos (Monitor)	Acid hydrolysis	Unknown degradation rate	O,S-dimethylphosphorothioic acid and ammonia are expected to be less toxic than Monitor.
	Alkaline hydrolysis	Complete degradation	Methyl mercaptan is moderately toxic. Salts of O-methylphosphoramidoate are expected to be less toxic than Monitor.
	Chemical oxidation	Complete degradation	The only known product is the sulfoxide $CH_3SS(O)_2CH_3$.
Disulfoton (Di-Syston)	Alkaline hydrolysis	Complete degradation	Alkaline salts of O,O-dimethylphosphorothioic acid and ethylthioethyl mercaptan are non-toxic.
	Acid hydrolysis	Slow degradation rate	Essentially the same products as alkaline hydrolysis.
Phorate (Thimet)	Alkaline hydrolysis	Complete degradation	Alkaline salts of O,S-diethylphosphorodithioate, formaldehyde, and ethyl mercaptan are non-toxic.
	Acid hydrolysis	Complete degradation	Essentially the same products as alkaline hydrolysis.
PennCap-M (Encapsulated methyl parathion)	Alkaline hydrolysis	Complete degradation	Alkaline salts of dimethylphosphorothiate are non-toxic; p-nitrophenol is slightly toxic, but far less toxic than methyl parathion.
	Acid hydrolysis	Slow degradation rate	Essentially the same products as alkaline hydrolysis.
	Chemical reduction	Unknown degradation rate	O,O-dimethyl-O-p-aminophenylphosphorothioate is non-toxic.
	Chemical oxidation	Complete degradation	Intermediate product methyl paraoxon is more toxic than methyl parathion. The oxon can hydrolyze to dimethyl phosphate and p-nitrophenol.

Table 13. Summary of Effects of Chemical Treatment on Pesticides for which Alkali Treatment is Recommended (Cont'd).

Pesticide	Chemical Treatment	Degree of Degradation	Identity and Environmental Hazard of Degradation Products
Carbofuran (Furadan)	Alkaline hydrolysis	Complete degradation	Carbonate and methylamine are non-toxic. The toxicity of 2,2-dimethyl-2,3-dihydrobenzofuran-7-ol is unknown but is expected to be of the same order as α-naphthol which is non-toxic.
	Acid hydrolysis	Slow reaction	Essentially the same products as alkaline hydrolysis.
Aldicarb (Temik)	Alkaline hydrolysis	Complete degradation	Carbonate, methylamine and β-methyl, β-thiomethylpropionaldehyde oxime are non-toxic. However, oximes are suspected carcinogens.
	Chemical oxidation	Complete degradation	Aldicarb sulfoxide is rapidly produced and it slowly oxidizes to aldicarb sulfone. Both the sulfoxide and sulfone are more toxic and are hydrolyzed faster than aldicarb.
Methomyl (Lannate, Nudrin)	Alkaline hydrolysis	Complete degradation	Carbonate, methylamine, and S-methyl-N-hydroxylthioacetamidate are non-toxic.
Captafol	Alkaline hydrolysis	Complete degradation	Hydrolysis products are not fungicidally active. Chloride and dichloroacetate are non-toxic and sulfide is slightly toxic. Tetrahydrophthalimide is not an acute toxicant but it is teratogenic. Tetrahydrophthalimide slowly hydrolyzes in base to yield the non-toxic, cyclohex-2-ene-1,2-dicarboxylic acid.
	Acid hydrolysis	Slow reaction	Essentially the same products as alkaline hydrolysis.

Table 14. Summary of Effects of Chemical Treatment on Pesticides for which No Chemical Treatment is Recommended.

Pesticide	Chemical Treatment	Degree of Degradation	Identity and Environmental Hazard of Degradation Products
Ronnel (Korlan, Fenchlorophos)	Weak alkaline hydrolysis	Complete degradation	Alkaline salts of desmethylfenchlorophos have unknown toxicities.
	Strong alkaline hydrolysis	Complete degradation	Alkaline salts of 0,0-dimethyl phosphorothioate and 2,4,5-trichlorophenol. The trichlorophenol is more toxic than ronnel.
Dimethoate (Cygon)	Alkaline hydrolysis	Complete degradation	Initial products are alkaline salts of 0,0-dimethylphosphorothioate and N-methyl α-mercaptoacetamide. The amide subsequently hydrolyzes to α-mercaptoacetic acid and methylamine. Mercaptoacetic acid is about as toxic as dimethoate.
	Acid hydrolysis	Complete degradation	Essentially the same products as alkaline hydrolysis.
Dyfonate	Alkaline hydrolysis	Unknown degradation rate	Initial products are alkaline salts of O-ethyl ethylphosphonothioate and phenyl mercaptan. Phenylmercaptan can oxidize to yield diphenyl disulfide. Phenyl mercaptan is toxic (oral LD_{50} of 46 mg/kg).
	Chemical oxidation	Complete degradation	The products probably include diphenyl disulfide. Intermediates include the more toxic oxon and possibly phenyl mercaptan.
Def	Alkaline hydrolysis	Slow degradation rate	Final products phosphoric acid salts and ethyl mercaptan are non-toxic.
	Acid hydrolysis	Slow degradation rate	Essentially the same as alkaline hydrolysis.
	Chemical oxidation	Complete degradation	Unknown products. One product appears to be dibutyl sulfide.

Table 14. Summary of Effects of Chemical Treatment on Pesticides for which No Chemical Treatment is Recommended (Cont'd).

Pesticide	Chemical Treatment	Degree of Degradation	Identity and Environmental Hazard of Degradation Products
EPTC (Eptam)	Alkaline hydrolysis	Slow reaction	Diisopropylamine and ethyl mercaptan are more toxic to rats than EPTC.
	Strong acid hydrolysis	Complete degradation	Diisopropylamine and ethyl mercaptan are more toxic to rats than EPTC.
	Chemical oxidation	Unknown	Di n-propylamine is non-toxic. No toxicity information for ethanesulfonic acid was found.
Molinate (Ordram)	Alkaline hydrolysis	Slow reaction	Hydrolysis product hexamethylenimine is more toxic than molinate.
Thiram	Chemical reduction by metals or sulfide	Complete degradation	Initial products are dimethyl dithiocarbamic acid salts, some of which are carcinogenic. When acidified, the salts degrade to diethylamine and carbon disulfide. Carbon disulfide is relatively non-toxic but is inflammable and has noxious organoleptic properties.
	Chemical reduction with cyanide ion	Complete degradation	Thiocyanate ion and the monosulfide have no evidence of carcinogenic effects.
	Chemical reduction with acetone or acetate	Complete degradation	Products include CS_2, COS, dimethylamine, and other products. CS_2 and COS are low boiling, inflammable, and have obnoxious organolepic properties.
Propanil	Acid or alkaline hydrolysis	Complete degradation	Propanoic acid is non-toxic; 2,4-dichloroaniline is slightly less toxic than propanil, but it is metabolized to persistent azobenzenes
Chloroxuron	Acid hydrolysis	Unknown hydrolysis rate	Carbon dioxide is non-toxic; methylamine is slightly toxic; and p(p-chlorophenoxyl)aniline toxicity is unknown.

Table 14. Summary of Effects of Chemical Treatment on Pesticides for which No Chemical Treatment is Recommended (Cont'd).

Pesticide	Chemical Treatment	Degree of Degradation	Identity and Environmental Hazard of Degradation Products
Diphenamid	Alkaline hydrolysis	Slow reaction	Phenylacetic acid and dimethylamine are less phytotoxic.
Simazine	Strong acid or alkaline hydrolysis	Complete degradation	Hydroxysimazine is not herbicidally active.
Cyanazine (Bladex)	Chemical hydrolysis	Unknown rate	Intermediate products include the products from -CN hydrolysis to amide and to acid. The chloride is also hydrolyzed to yield the hydroxy-*s*-triazene. Toxicities of these products are not available.
Aminotriazole (Amitrole)	Derivatization with ketones and aldehydes	Fast reaction	Effect on toxicity is unknown.
	Derivatization with aryl chlorides or anhydrides	Fast reaction	Effect on toxicity is unknown.
PCNB (Terrachlor)	Alkaline hydrolysis	Complete degradation	Pentachlorophenol and nitrate are formed. Pentachlorophenol is a toxic pesticide which should be disposed by ground disposal.
	Chemical reduction	Complete degradation	Pentachloroaniline toxicity is unknown.
DNBP (Dinoseb)	Chemical oxidation	Unknown reaction rate	Toxicity of dinitrobenzoic acid is not known. The use of the oxidants require technical skills by the user.
	Chemical reduction	Unknown reaction rate	Final products are amines. Intermediate products are unknown. Product toxicities are unknown.
	Alkylation	Unknown reaction rate	Toxicity of the products is unknown.

Table 14. Summary of Effects of Chemical Treatment on Pesticides for which No Chemical Treatment is Recommended (Cont'd).

Pesticide	Chemical Treatment	Degree of Degradation	Identity and Environmental Hazard of Degradation Products
Chloropicrin	Reaction with alkoxide	Complete degradation	Alkyl orthocarbonate esters, chloride, and nitrate are non-toxic.
	Heating with fuming sulfuric acid	Complete degradation	Phosgene and nitrosyl chloride are toxic.
	Heating with hydriodic acid	Complete degradation	Ammonia, carbon dioxide, hydrogen chloride, and iodine are less toxic than chloropicrin.
	Heating with iodide salts	Complete degradation	Carbon tetraiodide could be carcinogenic.
	Heating with ammonia	Complete degradation	Guanidine is non-toxic.
	Heating with sodium peroxide	Complete degradation	Carbonate, chloride, and nitrate salts of sodium are non-toxic.
	Reaction with mercaptide ion	Complete degradation	Disulfide and a mixture of carbon dioxide, nitrogen, carbon monoxide and nitrousoxide are the products. They are less toxic than chloropicrin.
	Reaction with trialkyl-phosphine	Complete degradation	Trialkylphosphonium dialkylphosphonium dichloride and a mixture of carbon dioxide, nitrogen, carbon monoxide, and nitrous oxide are the products. They are less toxic than chloropicrin.
	Heating with zinc plus acetic acid	Complete degradation	Methylamine and chloride ion are non-toxic.
Chlorobenzilate	Acid hydrolysis	Complete degradation	*p*-*p*'-dichlorobenzophenone oral toxicity is not known.
	Alkaline hydrolysis	Complete degradation	The initial product is sodium chlorobenzilate which hydrolyzes to *p*,*p*'-dichlorobenzophenone when acidified.

Table 14. Summary of Effects of Chemical Treatment on Pesticides for which No Chemical Treatment is Recommended (Cont'd).

Pesticide	Chemical Treatment	Degree of Degradation	Identity and Environmental Hazard of Degradation Products
2,4,5-T	Chlorinolysis at approximately 85°C	Partial degradation	Herbicidally inactive products. Their mammalian toxicity is unknown.
	Chlorinolysis above 400°C	Complete degradation	Carbon tetrachloride, phosgene and hydrogen chloride are toxic.
	Strong acid hydrolysis	Complete degradation	2,4,5-trichlorophenol is pesticidal. Formaldehyde is slightly toxic, but an irritant. Carbon dioxide is non-toxic.
	Reaction with alkali metals in liquid ammonia	Complete degradation	Unknown products.
	Photochemical reaction in hydrocarbon solution	Complete degradation	Degradation of the tetrachlorodioxin impurity in 2,4,5-T.
Endrin	Acid treatment at 100°C or thermal treatment	Complete degradation	Products are rearranged isomers: an alcohol, ketone, and aldehyde. They are less toxic than endrin.
	Photochemical treatment	Complete degradation	Products include those obtained from acid or thermal treatment, plus an additional production containing one carbon-chlorine bond reduced to a carbon-hydrogen bond.
	Treatment with sodium methoxide in dimethyl sulfoxide	Complete degradation	Reduction of one carbon-chlorine bond to a carbon-hydrogen bond. Product toxicity is not known.
	Reduction with metals or metal complexes	Slow reaction to complete degradation	Rearranged and dechlorinated products. Their toxicities are unknown.
Dibromochloropropane (DBCP)	Mild alkaline hydrolysis	Complete degradation	2-bromoallyl alcohol is a potential carcinogen.
	Strong alkaline hydrolysis	Complete degradation	Propargyl alcohol is more toxic than DBCP.

Table 14. Summary of Effects of Chemical Treatment on Pesticides for which No Chemical Treatment is Recommended (Cont'd).

Pesticide	Chemical Treatment	Degree of Degradation	Identity and Environmental Hazard of Degradation Products
Dibromochloropropane (Cont'd.)			
	Reaction with potassium ethoxide	Complete degradation	Ethyl propargyl alcohol is probably only mildly toxic.
	Alkali metals in liquid ammonia	Complete degradation	Products and their toxicities are unknown.
	Chemical reduction	Complete degradation	Products depend upon conditions. Final products are non-toxic hydrocarbons. Intermediates are halogenated propanes.
D-D	Mild alkaline hydrolysis	Complete degradation	1-chloroallyl alcohol is a potential carcinogen.
	Strong alkaline hydrolysis	Complete degradation	Propargyl alcohol is more toxic than D-D.
	Hydrolysis at 200°C or 150°C with PbO	Complete degradation	Acetone and propionaldehyde are non-toxic.
	Chemical reduction	Slow reaction	Products not specified.
Dicamba	Hydrolysis	No reaction	---
	Chemical oxidation	No reaction	---
	Alkali metal in ammonia	Complete degradation	Products are unknown.
MSMA	Chemical oxidation	Complete degradation	Arsenic acid is more toxic.
	Reaction with sulfide	Complete degradation	Methylarsenic disulfide is of unknown toxicity.
Arsenic acid	Reaction with sulfide	Complete degradation	Arsenic sulfide is a less hazardous precipitate.

Table 14. Summary of Effects of Chemical Treatment on Pesticides for which No Chemical Treatment is Recommended (Cont'd).

Pesticide	Chemical Treatment	Degree of Degradation	Identity and Environmental Hazard of Degradation Products
Sodiumfluoroacetate (Compound 1080)	Acid or alkaline hydrolysis	Very slow reaction	Fluoride ion is slightly toxic. No other products identified.
	Chemical oxidation	No reaction	—
Creosote	Chemical oxidation	Unknown reaction rate	Unknown reaction products.
Warfarin	Heating with alkali	Complete degradation	3-(o-hydroxyphenyl)-5-phenyl-2-cyclohexene-1-one. Toxicity unknown.
	Heating with acid in alcohols	Unknown reaction rate	Product ketal has unknown toxicity.
	Reaction with amines	Complete reaction	Schiff base derivatives are produced. Their toxicities are unknown.
BHC (HCH) (Lindane)	Alkaline hydrolysis	Complete degradation	Chloride and a mixture of trichlorobenzenes are formed. Chloride is non-toxic. Trichlorobenzenes are not acutely toxic and have no known long-term effects. They are, however, persistent and can potentially bioaccumulate.
	Chemical reduction	Complete degradation	Chloride is non-toxic. Benzene has a low acute toxicity but has given positive carcinogenic tests.
Paraquat	Alkaline hydrolysis	Unknown extent of degradation	An undefined resinous material of unknown toxicity is formed.
	Oxidation with hydrogen peroxide	Varies	Weak H_2O_2 yields the pyridone, dipyridone, 4-carboxyl-1-methyl-pyridinium ion, and possibly 4-carboxyl-1-methylpyridone; product toxicities are unknown. Strong oxidizing conditions yeild oxalic acid which is non-toxic, but reaction rate is unknown.
	Oxidation with aqueous permanganate, chlorine, or chlorine dioxide	Fast reaction	Products of chlorine dioxide reaction are ammonia and oxalic acid which are non-toxic. These are also postulated products from permanganate or chlorine oxidations, but have not been demonstrated. The chlorine oxidation requires pH greater than 11. Very high ratios of oxidant:paraquat are required.

The alternatives for their disposal have been discussed in Section 3. In order of prefered use the recommended disposal is: (1) incineration at a suitable facility (for all except the arsenicals); (2) disposal in a specially designated landfill; and (3) land burial, sometimes with chemical treatment. Proper facilities are scarce for the first two alternatives.

Alkaline hydrolysis is the only detoxification procedure recommended; the pesticides which can be hydrolyzed are members of the phosphorus-containing pesticides (monocrotophos; phosphamidon; fensulfothion; PennCap-M (microencapsulated methyl parathion); disulfoton; phorate; and methamidophos), carbamates (carbofuran, aldicarb, and methomyl), and captafol of the nitrogen-containing pesticides. Some chemical treatments which are potentially useful to reduce hazard of a few of the pesticides in land burial, should be tested. These treatments include precipitation of the arsenicals with divalent cations (e.g., calcium), acidification of dinoseb, dicamba and warfarin sodium to reduce leaching rate and mixing simazine and cyanazine with lime to assist degradation.

Recommendations for further study have been based on three problem areas: a disposal method has been derived from existing data from laboratory studies but has not been field tested; information suggests that a method is feasible but some data is lacking and no practical method can be recommended; and insufficient data is available to devise an approach. The following areas of research are recommended:

- Field test all recommended procedures in this study and the companion work (1).
- Examine the use of aqueous and ethanolic iodide containing solutions as detoxicants for phosphorus-containing pesticides.

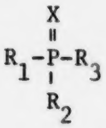
- Determine the hydrolysis kinetics for fensulfothion.
- Determine the hydrolysis products from dimethoate with strong caustic (1-2N NaOH).
- Determine the hydrolysis kinetics for methamidophos (Monitor) in aqueous acid.
- Evaluate a two step detoxification for Dyfonate consisting of alkaline hydrolysis followed by oxidation with household chlorine bleach.
- Determine toxicity and environmental fate of 2,2-dimethyl 2,3-dihydrofensofuran-7-ol which is produced by alkaline hydrolysis of carbofuran.
- Determine the toxicity of methyl N-hydroxyacetimidate which is produced by alkaline hydrolysis of methomyl.
- Evaluate zinc-acetic acid (or hydrochloric acid) as a detoxicant for chloropicrin, endrin, D-D, BHC, and DBCP.
- Evaluate iron salts as a detoxicant for endrin.
- Determine environmental fate and toxicity of the trichlorobenzenes produced from BHC (and lindane) hydrolysis in caustic.
- Evaluate alkanolamines as a detoxicant for DBCP.
- Evaluate if precipitation of MSMA or arsenic acid with sulfide or a suitable cation (Ca^{2+}, Mg^{2+}, or Fe^{3+}) yields a product acceptable for land disposal.
- Evaluate if the triazenes simazine and cyanazine can be adequately disposed by mixing with lime and land burial.
- Further evaluate alkaline hydrolysis and chemical oxidation for paraquat detoxification.

APPENDIX A

CHEMICAL METHODS FOR THE DEGRADATION/DETOXIFICATION OF PHOSPHORUS-CONTAINING PESTICIDES

A.1 GENERAL REVIEW OF APPLICABLE DISPOSAL METHODS

All the phosphorus-containing pesticides selected for this study are ester or amide derivatives of ortho-phosphoric acid or thiophosphoric acids ($H_3PO_{4-n}S_n$ where n = 0 to 3). The general structure of the selected pesticides is:



$$R_1-\overset{\overset{\displaystyle X}{\|}}{\underset{\underset{\displaystyle R_2}{|}}{P}}-R_3$$

where X is either O or S, $R_1 = R_2$ are usually either methoxide (CH_3O-) or ethoxide (C_2H_5O-) radical, and R_3 is an alcohol, phenol, mercaptan or amine group (8-10). Table 15 summarizes the selected organo-phosphorus pesticides and their chemical structures. The pesticides methamidophos (Monitor), Dyfonate, and Def differ slightly from the generalized structure, but their chemical reactivity remains fundamentally the same. Def is a phosphorotrithioate derivative ($R_1 = R_2 = R_3$ = n-butylmercaptide). Methamidophos is an amide containing mixed ester groups (methoxide and methyl mercaptide). Dyfonate is a phosphonodithioate (R_1 = ethyl).

The most important chemical detoxification method for the selected organophosphates is hydrolysis, which removes one of the ester groups to yield a phosphate diester. Shih and Dal Porto have discussed some characteristics of the phosphate hydrolysis (1). Their general discussion did not provide a suitable description of the kinetic and mechanistic problems. A complete description

Table 15. Chemical Structure of Selected Phosphorus-Containing Pesticides.

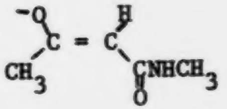
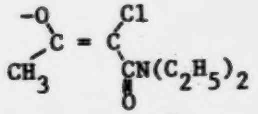
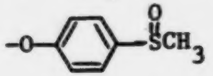
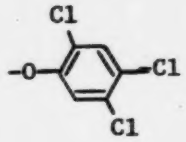
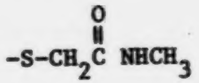
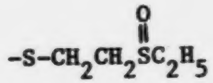
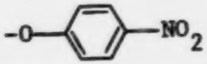
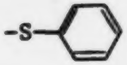
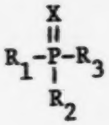
Pesticide Name		Structure[a]				Molecular Weight (g)
Common	Trade	X	R_1	R_2	R_3	
Monocrotophos	Azodrin	O	CH_3O	CH_3O		223.2
Phosphamidon	Dimecron	O	CH_3	CH_3O		299.7
Fensulfothion	Dasanit	S	C_2H_5O	C_2H_5O		308.3
Ronnel	Korlan	S	CH_3O	CH_3O		321.6
Dimethoate	Cygon	S	CH_3O	CH_3O	 $-S-CH_2\overset{O}{\overset{\|}{C}}\ NHCH_3$	229.2
Disulfoton	Di-Syston	S	C_2H_5O	C_2H_5O	 $-S-CH_2CH_2\overset{O}{\overset{\|}{S}}C_2H_5$	274.4
Phorate	Thimet	S	C_2H_5O	C_2H_5O	$-SCH_2SC_2H_5$	260.4
Methamidophos	Monitor	O	CH_3O	CH_3S	$-NH_2$	141.1
Def	DEF	O	C_4H_9S	C_4H_9S	$-S(CH_2)_3CH_3$	333.6

Table 15. Chemical Structure of Selected Phosphorus-Containing Pesticides (Cont'd).

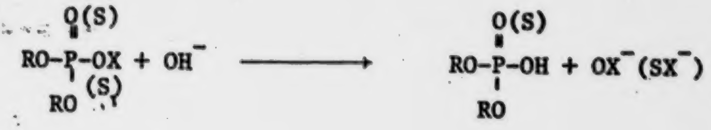
Pesticide Name		Structure[a]				Molecular Weight (g)
Common	Trade	X	R_1	R_2	R_3	
(Microencapsulated) Methylparathion	PennCap M	S	CH_3O	CH_3O		291.3
Dyfonate	Dyfonate	S	C_2H_5O	C_2H_5		246.3

a 

$$R_1-\overset{\overset{\displaystyle X}{\|}}{\underset{\underset{\displaystyle R_2}{|}}{P}}-R_3$$

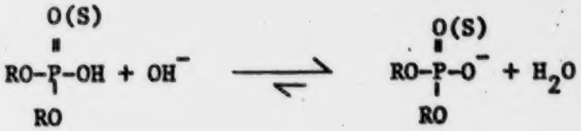
of phosphate hydrolysis is beyond the scope of this study, but a brief description of important parameters is presented.

Phosphate ester hydrolysis proceeds by several possible mechanisms (8-10). While Shih and Dal Porto have noted the existence of these differences, they neither fully described the possible effects on products nor on kinetics. Phosphate triesters can hydrolyze in acidic, neutral, or alkaline media. In alkaline media they react with hydroxide anion by a mechanism in which the rate determining step is rupture of the most acidic P-O (or P-S) bond. Since thiol, phenol and vinyl alcohols are more acidic than methanol or ethanol, the alkaline hydrolysis yields dialkyl phosphate esters (where R is methyl or ethyl):



$$\mathrm{RO{-}\underset{RO}{\overset{O(S)}{\overset{\|}{P}}}{-}\underset{(S)}{O}X + OH^-} \longrightarrow \mathrm{RO{-}\underset{RO}{\overset{O(S)}{\overset{\|}{P}}}{-}OH + OX^-(SX^-)}$$

Further reactions must be accounted for in alkaline hydrolysis. The dialkyl phosphates are strong acids, which will immediately form the corresponding anion within alkaline media:



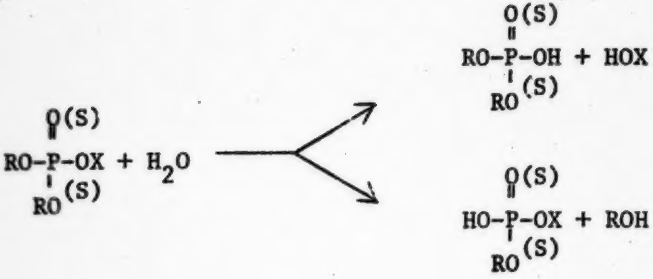
$$\mathrm{RO{-}\underset{RO}{\overset{O(S)}{\overset{\|}{P}}}{-}OH + OH^-} \rightleftharpoons \mathrm{RO{-}\underset{RO}{\overset{O(S)}{\overset{\|}{P}}}{-}O^- + H_2O}$$

and the cleaved anion has the equilibrium:

$$\mathrm{OX^-(SX^-) + H_2O} \xrightleftharpoons{K_{eq}} \mathrm{HOX(HSX) + OH^-}$$

The hydrolysis stoichiometry will vary with the equilibrium constant, K_{eq}, and ranges from 1:1 to 1:2 for phosphate triesters to hydroxide ratio. The dialkyl phosphate anion is stable to further hydrolysis except at very high pH (9, 10).

Phosphate triesters hydrolyze by a similar mechanistic sequence in neutral and acidic solutions. The ester reacts by rupture at the O-X (or S-X) bond. The salient feature of the neutral or acidic hydrolysis reactions is the product formation. Two phosphate diester products are possible:



Acid catalyzed reactions have several possible mechanistic pathways. The catalyzed reaction could proceed via protonation at a phosphate oxygen or within the ester group X. For further discussion a comprehensive text on phosphorus chemistry should be consulted (8-10). In general, when the product is a dialkyl phosphate, no further hydrolysis will occur above pH 1.5 (9). The stoichiometry of the phosphate triester hydrolysis in acid media involves only reaction of the ester and water, since protium ion, which is a true catalyst, is not consumed.

The time required for organophosphorus insecticide degradation can be calculated from published hydrolysis rate and the proper kinetic expression. The Handbook developed a kinetic expression which was not correct (1). Shih and Dal Porto derived an expression for calculating the time 50%, 99%, and

99.9% degradation from the kinetic expression:

$$\frac{dx}{dt} = k(a-x)(b-x) \qquad \text{A-1}$$

where a and b are the initial concentrations of organophosphorus pesticide and of hydroxide (or protium), respectively; x is the decrease in organophosphate pesticide concentration after time t; and k is the reaction rate constant. This rate equation errs in the stoichiometry of the hydrolysis (13, 14). Alkaline hydrolysis could utilize two or more moles of hydroxyl ion per mole of insecticide hydrolyzed. Also, the hydrolysis in acid media does not consume hydrogen ions. The rate expression will differ for the acid and alkaline hydrolyses. Equation A-1 implies that rate constant, k, is completely pH independent, which is not true (see the Shih and Dal Porto discussion on Chemical Methods for the Degradation/Detoxification of Diazinon) (1). A bell-shaped relationship between hydrolysis rate constants and pH for a series of organophosphorus insecticides has been demonstrated (13). This pH profile implies that several hydrolysis mechanisms operate and each has an unique rate constant. The scheme below can account for hydrolysis kinetics and mechanism:

$$A + OH^- \xrightarrow{k_1} \text{Products}$$

$$A + H_2O \xrightarrow{k_2} \text{Products}$$

$$A + H^+ \underset{}{\overset{K}{\rightleftharpoons}} HA^+ + H_2O \xrightarrow{k_3} \text{Products}$$

where A is the organophosphorus pesticide; K is the equilibrium constant for pesticide protonation; and k_1, k_2, and k_3 are the observed hydrolysis rate constants for reactions of pesticide with hydroxyl ion, of pesticide with water, and protonated pesticide with water, respectively. Since multiple mechanisms could operate at any of these three reactions, the observed rate constants k_1, k_2, and k_3 could be composites of several rate constants. Equation (A-2) describes kinetics for organophosphorus pesticide hydrolysis at any pH:

$$\frac{dx}{dt} = k_1 C_A C_{OH^-} + k_2 C_A C_{H_2O} + k_3 C_A C_{H^+} C_{H_2O} \qquad \text{A-2}$$

where C_A, C_{OH^-}, C_{H^+}, and C_{H_2O} are concentrations of the pesticide, hydroxyl ion, hydrogen ion and water, respectively (9). This equation reduces to the expression:

$$\frac{dx}{dt} = \left[\frac{k_1 K_w}{C_{H^+}} + k_2 + k_3 K C_{H^+}\right] C_A C_{H_2O} \qquad \text{A-3}$$

where K_w is the dissociation constant for water. Observed kinetic data (9, 13) suggest that at pH greater than 8 ($C_{H^+} < 10^{-8}$ molar), the term $k_1 \ K_w/C_{H^+}$ dominates and the term reduces to:

$$\frac{dx}{dt} = k_1 C_A C_{OH^-}. \qquad \text{A-4}$$

This can be expressed as Equation (A-5):

$$\frac{dx}{dt} = k_1 \ (a-x)(b-nx) \qquad \text{A-5}$$

where n is the number of equivalents of hydroxide consumed per mole of organophosphate degraded. Integration yields:

$$kt = \frac{1}{b-na}\left[\ln\left(\frac{a}{b}\right)\left(\frac{b-nx}{a-x}\right)\right] \qquad \text{A-6}$$

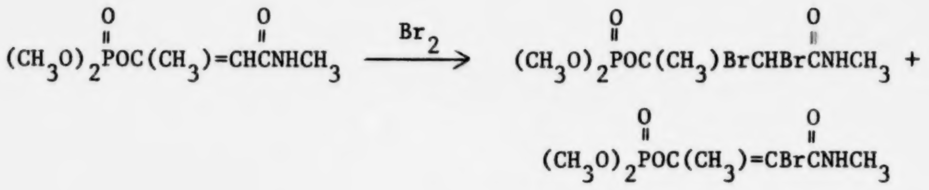
Equation (A-6) was used to calculate hydrolysis times. Equation (A-7) which was used to calculate the time for 99.9% ($t_{0.999}$) pesticide degradation is derived from Equation (A-7):

$$t_{0.999} = \frac{1}{(b-na)k}\ln\left(\frac{1000b - 999na}{b}\right) \qquad \text{A-7}$$

A.2 CHEMICAL METHODS FOR DETOXIFICATION OF MONOCROTOPHOS

Monocrotophos (Azodrin) is a systemic insecticide-acaracide which is used chiefly against cotton pests. It is miscible with water, soluble in acetone and alcohol, and very slightly soluble in kerosene and diesel fuel (14, 15). Azodrin is mostly marketed as a water miscible formulation containing 3.2 lb/gal but is also available as 5 lb/gal and as 80% wettable powder (15, 16).

Azodrin is relatively stable to heat; decomposition rate is 0.005, 0.02, and 0.085% per day at 20°, 30° and 40°C, respectively (17). It reacts with bromine to yield the dibromide and a bromovinyl analogue (18):



$$(CH_3O)_2\overset{\overset{O}{\|}}{P}OC(CH_3)=CH\overset{\overset{O}{\|}}{C}NHCH_3 \xrightarrow{Br_2} (CH_3O)_2\overset{\overset{O}{\|}}{P}OC(CH_3)BrCHBr\overset{\overset{O}{\|}}{C}NHCH_3 + (CH_3O)_2\overset{\overset{O}{\|}}{P}OC(CH_3)=CBr\overset{\overset{O}{\|}}{C}NHCH_3$$

Sodium iodide in acetone removes a methyl ester group and yields the desmethyl derivative (18). Methyl iodide is slightly toxic (oral LD_{50} = 220 mg/kg for rats) (4). Desmethyl monocrotophos is not an acetylcholinesterase inhibitor (8).

Kinetic and product data suggest that alkaline hydrolysis will yield non-toxic products in a reasonable time period; Table 16 summarizes salient kinetic data. Brown et al. describes products and kinetics (19); alkaline hydrolysis yields dimethyl phosphate, acetone, methylamine and carbon dioxide.

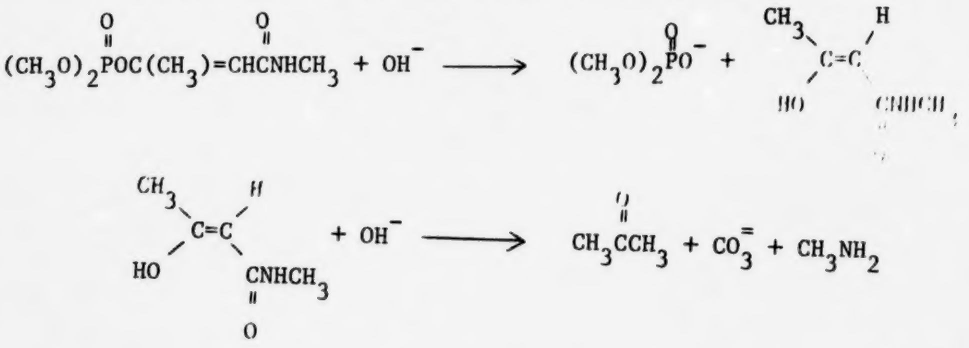


Table 16. Effect of pH and Temperature on the Hydrolysis of Monocrotophos.

Temperature	pH	Rate First order sec^{-1}	Rate Second order ℓ/(mole-sec)	Half life	Reference
100	3	$1.3x10^{-4}$	--	1.5 hr	Brown (19)
50	3	$1.1x10^{-6}$	--	180 hr	Brown (19)
100	4.6	--	--	80 min.	Zweig (18)
100	7	$5.2x10^{-4}$	--	0.37 hr	Brown (19)
50	7	$3.4x10^{-6}$	--	57 hr	Brown (19)
38	7	--	--	23 days	Zweig (18)
50	12	--	$0.75x10^{-2}$	--	Brown (19)
26	6.2	--	--	9% degradation in 1 wk	Seiber and Markel (20)

Since kinetic data was not found for monocrotophos hydrolysis at ambient temperature, the required time had to be estimated from the available data, Table 16. Several assumptions were necessary. It is assumed that the rate constants follow the Arrenhius Equation (21):

$$k = A\exp(-E_A/RT) \qquad \text{A-8}$$

where E_A is the activation energy, R is the gas constant, T is the absolute temperature and A is a constant. If E_A is known, the hydrolysis rate can be calculated at any temperature by Equation (A-9):

$$\log(k_1/k_2) = (0.219E_A)\ (1/T_2 - 1/T_1) \qquad \text{A-9}$$

Although Table 16 does not contain sufficient information to calculate an activation energy for the alkaline hydrolysis, a reasonable estimate can be derived. Gomaa _et_ _al_. have demonstrated that activation energies are similar for the acidic and basic hydrolyses of diazinon (21). It is assumed by reason of analogy that the acidic and basic hydrolyses of monocrotophos also have similar activation energies. Table 16 yielded activation energies of 22.8 and 24.1 kcal/mole for the pH 3 and pH 7 hydrolyses, respectively. With a 24 kcal/-mole activation energy assumed for the alkaline hydrolysis, the bimolecular rate constant at pH 12 was 0.32×10^{-3} l/mole-second. The time for 99.9% degradation ($t_{99.9}$) for its hydrolysis in strong base was calculated from Equation (A-7) with n = 1, since stoichiometry requires a minimum of 1:1 hydroxide to monocrotophos ratio. Table 17 presents calculated $t_{0.999}$ for monocrotophos using approximately four to five mole ratio of base to pesticide.

Table 17. Estimated Time for 99.9% Hydrolysis of Monocrotophos by 1N Sodium Hydroxide.

Formulation	Azodrin Content	With 1N NaOH Pesticide-Base Ratio	With 1N NaOH $t_{0.999}$ (Hours)	With 2N NaOH Pesticide-Base Ratio	With 2N NaOH $t_{0.999}$ (Hours)
3.2 lb/gal (watermiscible)	1.72 mole/liter	1:7 (vol/vol)	8.7	1:4 (vol/vol)	4.5
4.0 lb/gal (watermiscible)	2.18 mole/liter	1:10 (vol/vol)	8.0	1:5 (vol/vol)	3.5
80% wettable powder	1.63 mole/pound	1 lb:7ℓ	7.5	1 lb:3.5ℓ	3.2

Empty containers (bottles and drums) should be thoroughly drained then triple rinsed with a caustic rinse. Empty bags should be disposed by the EPA recommended procedures (Section 3) (7a).

A.3 CHEMICAL METHODS FOR DETOXIFICATION OF PHOSPHAMIDON

Phosphamidon (Dimecron) is a systemic insecticide-acaricide, which is applied to a wide variety of perennial and annual crops. It is marketed as a liquid (8 lbs/gal) and soluble concentrates (20, 50, and 100% weight volume). Phosphamidon is water miscible and soluble in most organic solvents except saturated hydrocarbons (14, 15, 22).

Phosphamidon is stable at room temperature and decomposes above 160°C. Nucleophiles such as iodide and mercaptide ion react at the methyl ester and yield desmethylphosphamidon (8, 17, 23). The product toxicities are expected to be similar to but less toxic than phosphamidon (Section A.2).

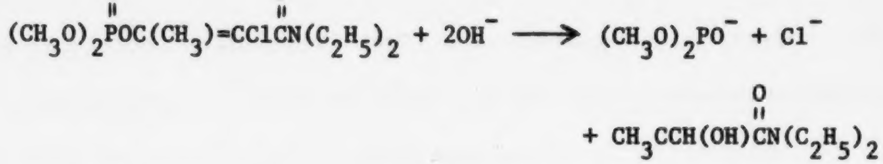
Aqueous hydrolysis appears to be a suitable detoxification procedure. Table 18 summarizes the published phosphamidon hydrolysis data. It is relatively stable in the pH range 2 to 8 but will hydrolyze fairly rapidly above pH 10. Phosphamidon actual consists of two geometrical isomers which hydrolyze at slightly different rates. The isomers differ by the geometry of the double bond; the methyl group and chloride can be cis or trans. The insecticide contains a cis- to trans- isomer ratio of approximately 70:30. The cis-isomer is the more reactive (23).

Hydrolysis products are pH dependent. Acidic hydrolysis yields α-chloroacetoacetic acid diethylamide (17). The amide can subsequently degrade to diethyl amine, carbon dioxide and chloroacetone in strong acid or with heating. A different series of products have been identified for the alkaline hydrolysis. Although the diethyl amide of α-chloroacetoacetic acid appears to initially form, it very rapidly hydrolyzes, even in weak alkaline solution, and yields chloride and the diethylamide of α-hydroxyacetoacetic acid (8, 24).

Table 18. Kinetic Data for Hydrolysis of Phosphamidon

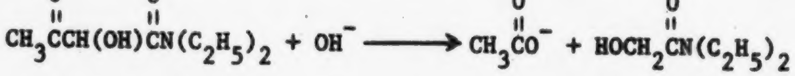
pH	Temperature, °C	Initial half-life	Reference
4	23	74 days	Anliker & Beriger (24)
4	45	6.6 days	Anliker & Beriger (24)
7	23	13.8 days	Anliker & Beriger (24)
7	45	2.1 days	Anliker & Beriger (24)
10	23	2.2 days	Anliker & Beriger (24)
10	45	3.3 hours	Anliker & Beriger (24)
10	27	cis=300 hours trans=100 hours	Bull *et al.* (25)
12	27	cis=2 hour trans=1 hour	Bull *et al.* (25)
Ethanol-pH 6 buffer (20:80)	70	Isomer I[a] = 10.5 hr	Ruzicka *et al.* (26)
	70	Isomer II[a] = 14 hr	Ruzicka *et al.* (26)

[a] Ruzicka *et al.* (26) report that Isomer II is apparently the major isomer.



$$(CH_3O)_2\overset{\overset{O}{\|}}{P}OC(CH_3){=}CCl\overset{\overset{O}{\|}}{C}N(C_2H_5)_2 + 2OH^- \longrightarrow (CH_3O)_2PO^- + Cl^- + CH_3CCH(OH)\overset{\overset{O}{\|}}{C}N(C_2H_5)_2$$

In strong alkali this amide can slowly hydrolyze to yield acetic acid and glycolic acid diethylamide. The product, glycolic acid, diethylamide is stable in base (26). The hydrolysis products are non-toxic and rapidly assimilated into natural constituents (25).



$$CH_3\overset{\overset{O}{\|}}{C}CH(OH)\overset{\overset{O}{\|}}{C}N(C_2H_5)_2 + OH^- \longrightarrow CH_3\overset{\overset{O}{\|}}{C}O^- + HOCH_2\overset{\overset{O}{\|}}{C}N(C_2H_5)_2$$

The hydroxide-phosphamidon stoichiometry for a complete hydrolysis requires some speculation. A 2:1 stoichiometry, the minimum required, yields the amide of α-hydroxyacetoacetic acid. Although the hydrolysis of this amide would increase the stoichiometry to a 3:1 ratio, data of Anlinker and coworkers suggest that its rate does not compete with phosphamidon hydrolysis (27). So, a 2:1 stoichiometry is considered the best estimate and $t_{0.999}$ is calculated from Equation (A-7) with $n = 2$. The bimolecular rate constant, k, can be estimated from the data of Bull _et al_. (25). Since their hydrolysis used low phosphamidon concentration (b>>a), Equation (A-10) can be derived for half-life from the general expression in Equation (A-6):

$$k = \frac{\ln 2}{C_{OH^-} t_{1/2}} \qquad \text{A-10}$$

k equal to 36 ℓ/mole-hour was calculated from the 2 hour half-life at pH 12 for _cis_-phosphamidon.

Table 19 summarizes approximate times for phosphamidon hydrolysis at ambient temperature using about 5-6 to 1 ratio of base to phosphamidon. Total degradation is achieved within 10 minutes using 2N aqueous sodium hydroxide. Empty containers should be decontaminated by the triple rinse using an alkaline rinse solution (Section 3).

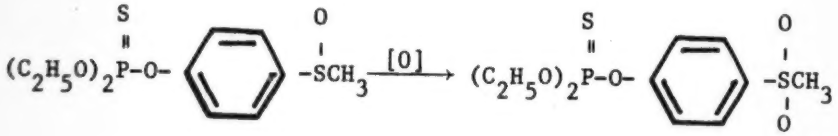
Table 19. Time Required for 99.9 Percent Phosphamidon Degradation with Aqueous Sodium Hydroxide at 27°C.

Formulation	Phosphamidon Content lb/gal	Phosphamidon Content moles/liter	With 1N NaOH Pesticide-Base Ratio (vol/vol)	With 1N NaOH $t_{0.999}$ (min.)	With 2N NaOH Pesticide-Base Ratio (vol/vol)	With 2N NaOH $t_{0.999}$ (min.)
Liquid	8	3.2	10:1	30.6	8:1	7.8
Soluble concentrate	10	4.0	15:1	24	10:1	7.8

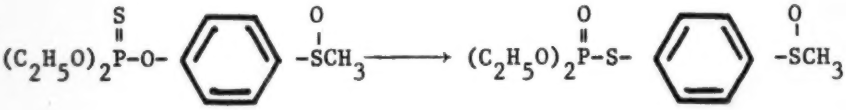
A.4 CHEMICAL METHODS FOR DETOXIFICATION OF FENSULFOTHION

Fensulfothion (Dasanit) is a nematocide-insecticide which is mainly employed in soil treatment. It is formulated as a spray concentrate (6 lbs/gal), 5%, 10%, and 15% granular, and 10% dust. Fensulfothion is slightly water soluble (1.6 g/ℓ) and soluble in most organic solvents with exception of saturated hydrocarbons (14, 15).

Chemical oxidants such as peroxides oxidize the sulfoxide group to sulfone (8)

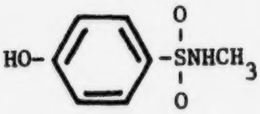


It also reacts by the thiono-thiolo rearrangement

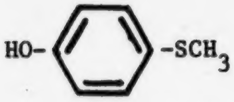


Both these reactions yield toxic products.

Although no direct information was found to describe hydrolysis rates or product toxicities, excellent data which exists for analogs was used as estimations for hydrolysis rates of fensulfothion. Its hydrolysis products are p-methylsulfinylphenol and 0,0-diethyl phosphorothioic acid (8). The diester of phosphorothioic acid is non-toxic. Although no toxicological data was found for p-methylsulfinylphenol, oral toxicity (rats) for the analogous p-(N-methylsulfamoyl) phenol is low, LD_{50} = 2500 mg/kg (4). If it is safe to assume that

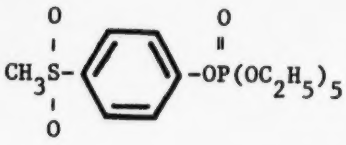


p-(N-methylsulfamoyl)phenol



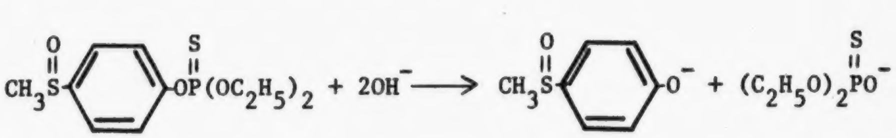
p-methylsulfinyl phenol

p-methylsulfinylphenol has an oral toxicity of the same magnitude, then fensulfothion hydrolysis products are non-toxic. Muhlman and Schrader described kinetics for an oxon analog, Preparation S-776, (13).



Oxons have a greater susceptibility to hydrolysis than corresponding thions. Hydrolysis rate constants for the thions are within a factor of ten of the oxons (10, 13). Table 20 summarizes kinetic data for Preparation S-776; the pH dependence of hydrolysis rate is typical of organophosphate pesticides. Alkaline hydrolysis at room temperature appears a feasible approach.

Time for 99.9% degradation, $t_{0.999}$, was calculated from Equation (A-7). Overall stoichiometry of 2:1 hydroxide-fensulfothion will account for hydrolysis and neutralization of acidic products:



The rate constant, k, for ambient temperature, ca. 25°C, was estimated from the data in Table 20. Activation energy was calculated as 22.4 kcal/mole from the Arrhenius relationship, Equation (A-9). Applied to kinetic data for pH 9,

Table 20. Kinetic Data for the Hydrolysis of S-776 (Analog of Fensulfothion). From Muhlman and Schrader (13).

Temperature, °C	pH	k $(\text{hours}^{-1})\text{x}10^2$	Half-life
0	1-5	$5.4\text{x}10^{-4}$	5350 days
10	1-5	$2.4\text{x}10^{-3}$	1200 days
20	1-5	$9\text{x}10^{-3}$	320 days
30	1-5	$3.1\text{x}10^{-2}$	93 days
40	1-5	$1.0\text{x}10^{-1}$	29 days
50	1-5	$3.0\text{x}10^{-1}$	9.6 days
60	1-5	$9.0\text{x}10^{-1}$	3.2 days
70	1-5	2.40	1.2 days
70	nHCl	8.38	8.3 hours
70	1	3.56	19.5 hours
70	2	3.11	22.3 hours
70	3	3.06	22.6 hours
70	4	3.36	20.6 hours
70	5	3.56	19.5 hours
70	6	4.48	15.5 hours
70	7	8.0	8.7 hours
70	8	8.17	8.5 hours
70	9	25.6	2.7 hours

values of 1.84×10^{-3} hour^{-1} and 3.07 l/mole-min. were obtained for the pseudo-first order (k_1) and second order rate constants (k_2), respectively, for Preparation S-5776 (Equation A-11). The approximate $t_{0.999}$ of fensulfothion was calculated with an estimated second order rate of 0.31 ℓ/mole-min., which is an order of magnitude less than for Preparation S-776.

$$k_2 = k_1/C_{OH^-} \qquad \text{A-11}$$

The estimated $t_{0.999}$ values are summarized in Table 21. Sodium hydroxide in 50% aqueous ethanol should be used for the hydrolysis, since the fensulfothion is only slightly soluble in water. The minimum degradation time for the spray concentrate is about 20 minutes with 2N base. The minimum time for granular and dust formulations which was estimated at approximately one-half hour requires additional time for the active ingredient to desorb into solution.

Empty containers should be thoroughly drained and then treated with a caustic rinse. Since aqueous solubility for fensulfothion is low, caustic in 50% aqueous ethanol is suggested. Empty bags should be disposed by the EPA recommended procedures (Section 3) (7a).

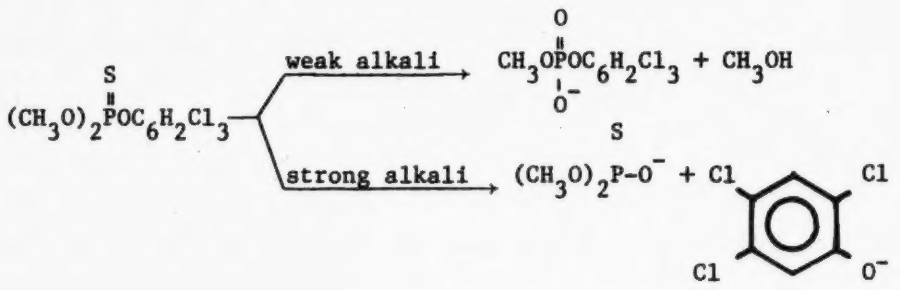
Table 21. Estimated Time Required for 99.9 Percent Fensulfothion Degradation with Sodium Hydroxide in 50% Aqueous Ethanol.

			With 1N NaOH		With 2N NaOH	
Formulation	Fensulfothion Content		Pesticide-Base Ratio	$t_{0.999}$ (min.)	Pesticide-Base Ratio	$t_{0.999}$ (min.)
Spray concentrate	6 lb/gal	2.32 mole/ℓ	12:1 (v/v)	37.1	6:1 (v/v)	19.8
Granular	15%	0.22 mole/lb	1.2 ℓ/lb	28.1	--	--
Granular	10%	0.15 mole/lb	0.6 ℓ/lb	28.1	--	--
Dust	10%	0.15 mole/lb	0.6 ℓ/lb	28.1	--	--

A.5 CHEMICAL METHODS FOR DETOXIFICATION OF RONNEL

Ronnel (fenchlorophos, Korlan) is used as an animal systemic and a structural, residual spray insecticide. It's formulations include emulsifiable concentrate (2 and 4 lb/gal) and 50% granular. Ronnel is stable at ambient temperature, but decomposes above 80°C. Solubility is 44 ppm (14, 15).

Although ronnel hydrolyzes relatively rapidly, the products hydrolysis remain relatively toxic. Cowart *et al*. determined ronnel loss in distilled water (pH approximately 6) (29). At ambient temperature apparent degradation was 40% at 2 days and 95% at one week. Ruzicka *et al*. reported half-life of 10.4 hours for ronnel hydrolysis at 70° in 80% pH 6 buffer - 20% ethanol (26). Hydrolysis products vary with alkaline content, while weak caustic hydrolyzes ronnel at the methyl ester, strong alkali cleaves the phenolic ester group (30).



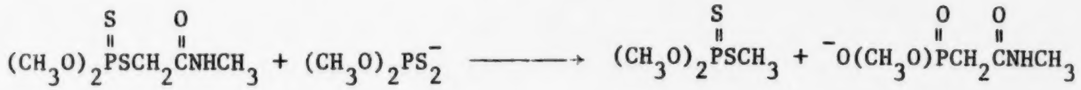
The strong alkali hydrolysis product, 2,4,5-trichlorophenol is more toxic than ronnel, oral LD_{50} of 802 mg/kg and 906 mg/kg, respectively for rats (4).

Ronnel should be disposed by a non-chemical method. The EPA recommended procedures should be followed (7a). Containers emptied of ronnel should be cleaned by the NACA recommended triple rinse method with water. Aqueous caustic which is generally recommended for the organophosphorus pesticides should not be used, because of the higher toxicity of 2,4,5-trichlorophenol.

A.6 CHEMICAL METHODS FOR DETOXIFICATION OF DIMETHOATE

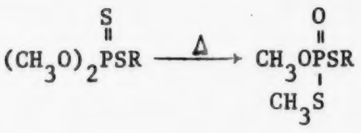
Dimethoate (Cygon) is a systemic insecticide-acaricide with a wide range of applications, including agricultural crops, ornamental plants, and house fly control (14, 15). It is soluble in alcohols and ketones, less soluble in aliphatic and aromatic hydrocarbons. Aqueous solubility is listed as 25 g/ℓ by Martin and Worthing (15) and 39 g/ℓ by Melnikov (28). Most dimethoate is formulated as 23.4% (2 lbs/gal) and 43.5% (9 lbs/gal) emulsifiable concentrate and 25% wettable powder. It is also formulated as an ULV concentrate (31).

Dimethoate toxicity is potentiated by reactions during its storage (28, 31). It reacts with O,O-dimethyl phosphorodithioate to yield desmethyl-dimethoate and the methylmercaptide ester:



$$\mathrm{(CH_3O)_2\overset{S}{\overset{\|}{P}}SCH_2\overset{O}{\overset{\|}{C}}NHCH_3 + (CH_3O)_2PS_2^- \longrightarrow (CH_3O)_2\overset{S}{\overset{\|}{P}}SCH_3 + {}^-O(CH_3O)\overset{O}{\overset{\|}{P}}CH_2\overset{O}{\overset{\|}{C}}NHCH_3}$$

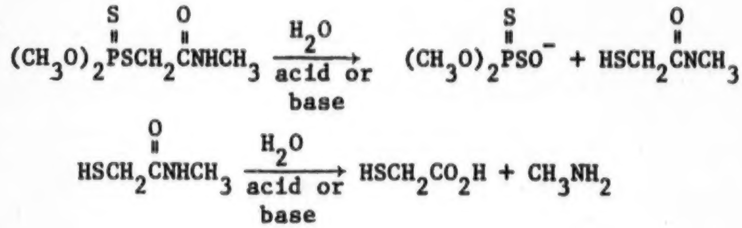
When it is heated, dimethoate yields a more toxic isomer by the thiono-thiolo rearrangement:



$$\mathrm{(CH_3O)_2\overset{S}{\overset{\|}{P}}SR \xrightarrow{\Delta} CH_3O\underset{\underset{CH_3S}{|}}{\overset{O}{\overset{\|}{P}}}SR}$$

Oral LD_{50} values for rats have varied in the literature over the range 147 to 600 mg/kg. This wide range has been attributed to these reactions and possibly other similar reactions (8, 28, 31, 32).

Dimethoate can potentially hydrolyze with bond breakage at the dithiophosphate or carbamate portions of its structure. Dimethoate hydrolyzes in two steps to ultimately yield methylamine, mercaptoacetic acid and phosphorothioate derivatives (8, 23, 31). The kinetics follow the expected pH dependence for organophosphate hydrolysis: at 70°C half-lives were 0.8, 12, and 21 hours for pH 9, 6, and 2, respectively (10). Hydrolysis initiates by P-S bond clevage to yield N-methyl mercaptoacetamide (33, 34). The amide subsequently hydrolyzes and yields mercaptoacetic acid and methylamine. The half-lives reported for the hydrolysis account only for actual dimethoate degradation.



$$(CH_3O)_2\overset{S}{\overset{\|}{P}}SCH_2\overset{O}{\overset{\|}{C}}NHCH_3 \xrightarrow[\text{acid or base}]{H_2O} (CH_3O)_2\overset{S}{\overset{\|}{P}}SO^- + HSCH_2\overset{O}{\overset{\|}{C}}NCH_3$$

$$HSCH_2\overset{O}{\overset{\|}{C}}NHCH_3 \xrightarrow[\text{acid or base}]{H_2O} HSCH_2CO_2H + CH_3NH_2$$

Incomplete and conflicting information complicates assessment of hydrolysis as a detoxification method. The broad oral LD_{50} range reported for dimethoate contributes to the evaluation problems. An oral LD_{50} range of 150 to 250 mg/kg is assumed to best represent the toxicity of technical dimethoate. The products O,O-dimethyl phosphorothioate and methylamine are less toxic and not a problem. The initial hydrolysis product N-methyl mercaptoacetamide appears to be less toxic than dimethoate. Although an oral LD_{50} was not found for this product, the parent compound, mercaptoacetamide, has an intraperitoneal LD_{Lo} of 300 mg/kg for rats. If toxicity of the N-methyl amide can safely be estimated from this value, it is less toxic than technical dimethoate.

When the mercaptoacetic acid amide further hydrolyzes, it forms mercaptoacetic acid and methylamine as the terminal products. The oral LD_{50} of the mercaptoacetic acid is 250 mg/kg for rats, which is about as toxic as dimethoate. In conclusion, alkaline hydrolysis is not clearly delineated. Since one of the hydrolysis products is about as toxic as dimethoate, hydrolysis is judged not suitable for detoxification.

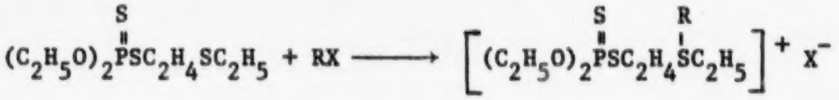
Dimethoate was oxidized with reagents such as bromine, iodine, and ceric ion to produce orthophosphate in an analytical scheme (25). Organic products were not identified.

Waste dimethoate should be disposed in an appropriate, non-chemical procedure; the EPA recommended procedures should be followed. Empty glass and metal containers should be triple-rinsed by the NACA recommended method (Section 3) (7a).

A.7 CHEMICAL METHODS FOR CHEMICAL DETOXIFICATION OF DISULFOTON

Disulfoton (Di-syston) is an insecticide applied at seeding and used as a folliar spray. It is formulated mainly as granules (2, 5, and 10%), and also available as liquid concentrate, seed treatment powder, and is combined in fertilizer. Disulfoton is soluble in most organic solvents and has a water solubility of 25 mg/ℓ (14, 15).

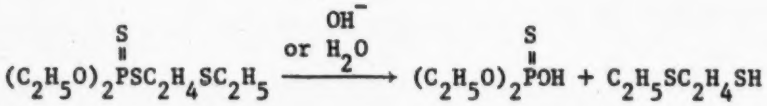
The mercaptide sulfur in disulfoton reacts with alkylating agents (such as methyl halides and methyl sulfate) and oxidants, but products are about as toxic as disulfoton. The reaction with alkylating agents yields S-alkyl sulfonium salts (8, 28):



$$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}SC_2H_4SC_2H_5 + RX \longrightarrow \left[(C_2H_5O)_2\overset{S}{\overset{\|}{P}}SC_2H_4\overset{R}{\overset{|}{S}}C_2H_5\right]^+ X^-$$

Disulfoton is oxidized to the corresponding sulfoxide and sulfone, and the phosphorothioate (8).

Although disulfoton is structurally similar to phorate, its hydrolysis products differ (Appendix A.8). Its hydrolysis product, ethylthioethyl mercaptan, is not further degraded under normal hydrolysis conditions (18, 35):



$$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}SC_2H_4SC_2H_5 \xrightarrow{\substack{OH^- \\ \text{or } H_2O}} (C_2H_5O)_2\overset{S}{\overset{\|}{P}}OH + C_2H_5SC_2H_4SH$$

No toxicity information was found for ethylthioethyl mercaptan. Its toxicity was estimated from available information on the parent compound, ethanedithiol

(HSC_2H_4SH); LD_{Lo} is 100 mg/kg for subcutanaceous toxicity for mice (4). Ethanedithiol toxicity is substantially less than disulfoton and it is assumed that ethylthioethyl mercaptan is also less toxic. Diethyl phosphorothioic acid is relatively non-toxic (4).

Disulfoton is more susceptable to alkaline than to acid hydrolysis. Ruzicka et al. report a half-life of 32 hours in 1:4 ethanol-pH 6 buffer (26). Muhlman and Schrader have evaluated pseudo-first order kinetics in water from pH 1 to 9 at 70°C and at pH 1-5 in temperature range from 0° to 90°C, Table 22 (13). The second order rate constant for ambient temperature hydrolysis was calculated by use of the Arrhenius relationship as discussed in Appendix A.2 (Equation A-9). Table 22 yielded an activation energy, E_A, of 24.2 kcal/mole and a second order rate constant of 4.5×10^3 ℓ/mole-hour (or 75 ℓ/mole-minute) at 25°C.

The complete hydrolysis of disulfoton requires an equimolar ratio of pesticide and hydroxide. Thiols are very weak acids and should not appreciably consume base. At least 4 mole excess of hydroxide is suggested to insure complete hydrolysis. A decontaminant of 1N sodium hydroxide in 50% aqueous ethanol is recommended, since disulfoton is only slightly soluble. The time for 99.9% hydrolysis, $t_{0.999}$, was calculated at less than 1 minute by Equation A-7. Since the disulfoton is formulated as granules, the hydrolysis first requires desorption and dissolution of the disulfoton; at least a 2 hour contact period is suggested with frequent stirring. The residue should be land buried in an area which will not affect water supplies. Empty containers should be thoroughly emptied and disposed in a safe manner (Section 3) (7a).

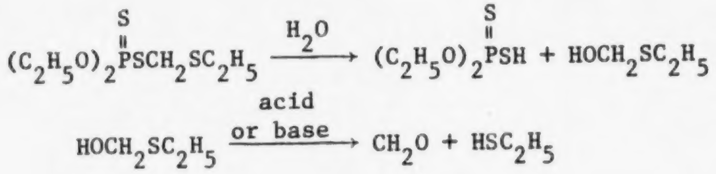
Table 22. Kinetic Data for the Hydrolysis of Disulfoton in Water. From Muhlman and Schrader (13).

Temperature, °C	pH	$k(10^2\ \text{hour}^{-1})$	Half-life
70	nHCl	2.88	24 hours
	1	1.11	62 hours
	2	1.11	62 hours
	3	1.10	62 hours
	4	1.11	62 hours
	5	1.16	60 hours
	6	1.56	44 hours
	7	2.50	27.6 hours
	8	3.22	21.5 hours
	9	9.61	7.2 hours
0	1-5	1.2×10^{-4}	232000 days
10	1-5	6×10^{-4}	4830 days
20	1-5	2.6×10^{-3}	1100 days
30	1-5	0.001	290 days
40	1-5	0.037	78 days
50	1-5	0.12	24 days
60	1-5	0.37	7.8 days
70	1-5	1.06	2.7 days

A.8 CHEMICAL METHODS FOR DETOXIFICATION OF PHORATE

Phorate (Thimet) is applied as a soil and systemic insecticide. It is available as a liquid concentrate (6 lbs/gal) and granular formulation (10% and 15%). Its solubility in water is relatively low (50 ppm). It is miscible with xylene, carbon tetrachloride, alcohols, ethers, and esters (14, 15, 36).

Phorate is susceptable to hydrolysis. Its hydrolysis apparently initiates with C-S cleavage to yield ethylthiomethanol and in a second step this product hydrolyzes to yield formaldehyde and ethyl mercaptan (37).



$$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}SCH_2SC_2H_5 \xrightarrow{H_2O} (C_2H_5O)_2\overset{S}{\overset{\|}{P}}SH + HOCH_2SC_2H_5$$

$$HOCH_2SC_2H_5 \xrightarrow[\text{or base}]{\text{acid}} CH_2O + HSC_2H_5$$

These hydrolysis products are all significantly less toxic than phorate: oral LD_{50} (for rats) are 4510, 682, and 800 mg/kg for the diethyl ester of phosphorodithioic acid, ethyl mercaptan, and formaldehyde, respectively (4). Organoleptic properties of ethyl mercaptan might be a nuisance; it has an obnoxious odor (38).

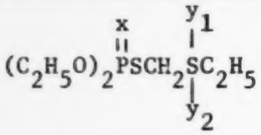
Hydrolysis half-lives at 70°C are 2 hours at pH 8 and 1.75 hours in (1:4) ethanol-pH 6 buffer solution, respectively (26, 28). Muhlman and Schrader described effect of temperature on acid catalyzed hydrolysis, Table 23 (13). Bowman and Casida report a pseudo-first order rate constant of $1.1x10^{-5}$ $min.^{-1}$ for hydrolysis at 28°C in 95% ethanol-0.1M aqueous bicarbonate (1:9) containing 500 mg/ℓ Triton X (32). Oxidized analogues are hydrolyzed more rapidly than phorate, but they are more toxic, Table 24.

Table 23. Effect of Temperature on Hydrolysis Rate of Phorate.[a] From Muhlmann and Schrader (13).

Temperature, °C	k $(\text{hour}^{-1})\times 10^2$	Half-life (hours)
0	0.014	200
10	0.08	36
20	0.4	72
30	1.83	1.6
40	7.14	0.4

[a] pH 1-5 in water.

Table 24. Hydrolysis Rates and Toxicity of Phorate and O-analogs.[a]



$$(C_2H_5O)_2\overset{x}{\overset{\|}{P}}SCH_2\underset{\substack{| \\ y_2}}{\overset{\substack{y_1 \\ |}}{S}}C_2H_5$$

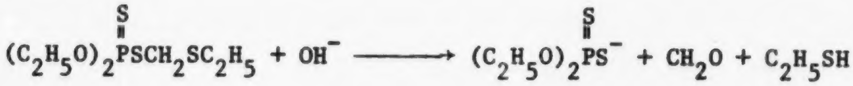
y	y_1	y_2	LD_{50}[b] (mg/kg)	k[c] ($min.^{-1}$)
S	-	-	8-10	$0.11x10^{-3}$
S	O	-	2-4	$13x10^{-3}$
S	O	O	1.8-2.0	$15x10^{-3}$
O	-	-	0.6-0.8	$6.6x10^{-3}$
O	O	-	1.4-1.6	0.28
O	O	O	0.6-0.8	0.35

[a] Bowman and Casida (37)

[b] Oral LD_{50} for rats

[c] Rate for 25 mg pesticide, 25 mg Triton X in 5 ml 95% ethanol plus 45 ml of aqueous 0.1M sodium carbonate at 28°C.

Alkaline hydrolysis is considered the best available detoxification procedure. The pH of the ethanolic buffer used by Bowman and Casida is estimated between 8.0 and 8.5 (39). Using the estimate of pH 8.5, the bimolecular rate constant of 80 ℓ/mole-sec. was calculated using Equation (A-11). Since phorate is relatively water insoluble, 50% aqueous ethanol is recommended as solvent. Stoichiometry is about 1:1 phorate to hydroxide:



$$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}SCH_2SC_2H_5 + OH^- \longrightarrow (C_2H_5O)_2\overset{S}{\overset{\|}{P}}S^- + CH_2O + C_2H_5SH$$

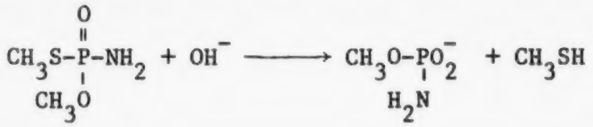
A four to five mole excess of hydroxide is suggested as a margin of safety. The time for 99.9% degradation, $t_{0.999}$, was calculated by Equation (A-7) with $n = 1$ at less than 1 minute. Additional time is suggested to allow for dissolution and mixing.

Container decontamination with an alkaline rinse is suggested. American Cyanamid recommends using an aqueous detergent rinse similar to the procedure described in Table 12 (36). Although phorate has a relatively low water solubility, it hydrolyzes so rapidly that aqueous caustic should be sufficient for detoxification. This contrasts with recommendations for other hydrolyzable pesticides of low solubility (Section 3). Empty bags should be disposed as recommended by the EPA (7a).

A.9 CHEMICAL METHODS FOR DETOXIFICATION OF MONITOR

Monitor (methamidophos) is a systemic broad-spectrum insecticide which is used mainly for vegetable crops. It is marketed as a 4 lb/gal liquid concentrate. Monitor is soluble in water (9 g/100 ml at 20°C), alcohols, and chlorinated aliphatic hydrocarbons (14, 15).

Hydrolysis products of Monitor are expected to be pH dependent. Although no specific information was found for its acid hydrolysis, phosphoramidic acid derivatives as a class will hydrolyze by P-N bond cleavage (9, 41). Monitor would yield O,S-dimethyl phosphorothioate and ammonia. Quistad and coworkers have examined the alkaline hydrolysis and found that Monitor produced methyl phosphoramidoate and methyl mercaptan (42):



$$CH_3S-\overset{\overset{O}{\|}}{\underset{\underset{CH_3O}{|}}{P}}-NH_2 + OH^- \longrightarrow CH_3O-\underset{\underset{H_2N}{|}}{PO_2^-} + CH_3SH$$

The reaction proceeds with a pseudo-first order rate constant of 3.2×10^{-2} min^{-1} at 30°C in a pH 11.5 buffer, which corresponds to a second order rate constant of 10.16 ℓ/mole-min (from Equation A-11). The hydrolysis products are expected to have significantly less hazards. Methyl mercaptan is a gas at ambient temperature, boiling point 7.6°C with an aqueous solubility of 23.3 g/ℓ. Its acute oral and inhalation toxicities are rated moderate (38). The hazard of O-methylphosphoramidate is expected to be significantly less than Monitor. Although its toxicity is not known, phosphoramidic salts are no longer acetylcholinesterase inhibitors (8, 41).

Acid hydrolysis is expected to cleave the P-N bond (9, 41). The expected hydrolysis products are O,S-dimethylphosphorathioate and ammonia. Both products are non-toxic (4). However, no hydrolysis rate information was found.

Monitor is oxidized by m-chloroperbenzoic acid in dichloromethane. The only product identified was $CH_3SS(O_2)CH_3$ (43).

Alkaline hydrolysis is recommended as a method of reducing Monitor's hazard. Since the hydrolysis stoichiometry requires 1:1 hydroxide to Monitor ratio, the 99.9% degradation time, $t_{0.999}$, is calculated from Equation (A-7) with n = 1. Complete hydrolysis of the 4 lb/gal (3.4 mole/ℓ) formulation with 8:1 (v/v) of 2N aqueous sodium hydroxide requires less than 1 minute. Containers should be thoroughly drained and rinsed with aqueous alkali (Section 3).

A.10 CHEMICAL METHODS FOR DETOXIFICATION OF DEF

Def is applied as a cotton defoliant. It is marketed as a 6 lb/gal emulsifiable concentrate. Def is not water soluble, but is soluble in organic solvents, including alcohols, chlorinated hydrocarbons, aliphatic and aromatic hydrocarbons (8, 14, 15).

Def can be hydrolyzed in strong acid or base to yield non-toxic products, but it is stable in the neutral pH range. Hydrolysis studies found in the literature study have described techniques by which Def is degraded to butyl mercaptan and phosphoric acid.

$$(\underline{n}\text{-}C_4H_9S)_3PO \xrightarrow[H_2O]{\text{acid or base}} 3\ \underline{n}\text{-}C_4H_9SH + H_3PO_4$$

Russian workers have used nitric acid in combination with either silver nitrate or hydrochloric acid (44). Alkaline conditions were also developed to exhaustively hydrolyze Def (45, 46). Barber and Boyd describe exhaustive hydrolysis of the analogous tributyl phosphorotrithioite, $(n\text{-}C_4H_9S)_3P$, which also apply to Def hydrolysis (46, 47). The conditions require one-half hour reflux with a 1:1 mixture of isopropyl alcohol and 0.5N sodium hydroxide plus 0.5% of sodium borohydride. No information was found which describe hydrolysis at ambient temperature with concentrations of 5 to 10% sodium hydroxide. The Def hydrolysis to phosphoric acid (and salts) and n-butyl mercaptan would be a suitable detoxification. Oral LD_{50} for rats was 1530 mg/kg and 682 mg/kg for the acid and mercaptan, respectively (4). The mercaptan does have an odor which is objectionable (38), but the odor can be controlled with hypochlorite solution (46); butyl mercaptan is probably converted to dibutyl sulfide (48).

Available literature suggests that Def hydrolyzes slowly in 1-2N alkali (15, 45). Although no suitable data was found for Def or analogous phosphorotrithioate esters, a lower limit reaction time can be speculated using data for trimethylphosphate hydrolysis. Sulfur analogs are hydrolyzed more slowly than corresponding phosphates (9, 10). Faust and Gomaa have indicated P=O esters hydrolyze at a rate 5 times faster than P=S analogs (10). Steric effects will result in slower hydrolysis for butyl esters than methyl esters (48). It is estimated that Def will have a rate constant at least one order of magnitude slower than trimethyl phosphate. Since the rate constant for trimethyl phosphate hydrolysis at 35°C is 0.330×10^{-3} ℓ/mole-sec. (11), the maximum rate for Def is estimated at 3×10^{-5} ℓ/mole-sec. A lower limit for $t_{0.999}$, 99.9% degradation time, was estimated from Equation A-7. Since the dissociation constant, K_{eq}, for $HPO_4^{=}$ hydrolysis to $PO_4^{\equiv}$ is 2.2×10^{-3} ℓ/mole, the reaction stoichiometry is expected to fall between 2 and 3. So $t_{0.999}$ was calculated for n = 2 and 3. The hydrolysis conditions were 1:10 (vol/vol) of

$$(C_2H_5S)_3P{=}O + 3OH^- \longrightarrow 3C_2H_5SH + PO_4^{\equiv}$$

$$PO_4^{\equiv} + H_2O \rightleftharpoons HPO_4^{=} + OH^-$$

6 lb/gal Def (2.29 mole/ℓ) reacted with 2N sodium hydroxide. The calculated $t_{0.999}$ was about 50 hours for n = 3 and 44 hours for n = 2. These hydrolysis times are judged too long for practical application.

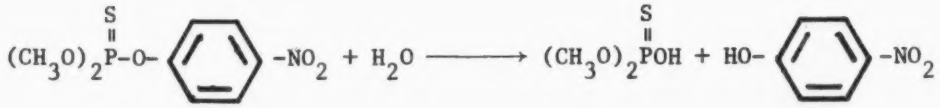
Def should be disposed by a non-chemical alternative; the EPA recommended procedures should be used (7a). The empty containers should be thoroughly drained and rinsed by the NACA recommended method (Section 3) (7a).

A.11 CHEMICAL METHODS FOR DETOXIFICATION OF PENNCAP-M

PennCap-M is a microencapsulated formulation of methyl parathion. The commercial product consists of an aqueous slurry of polyamide particles (30-50 μm average size) containing the active ingredient; the formulation contains 22.00% (2 lb/gal) methyl parathion. The product is registered for use in a wide variety of grains, fruits and vegetables, pasture, cotton and tobacco (49, 50).

Shih and Dal Porto have discussed salient information on physical and chemical properties of methyl parathion and its solubility (1). Methyl parathion is highly soluble in aromatic hydrocarbons and most organic solvents, but it is only slightly soluble in aliphatic hydrocarbons and almost insoluble in water (55-60 mg/ℓ) (15). Table 25 summarizes the hydrolysis rate information described in the Handbook (1).

Hydrolysis in water or alkaline medium yields O,O-dimethylphosphorothioic acid and p-nitrophenol:



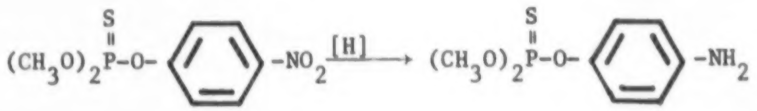
Shih and Dal Porto overestimated the toxicity of the products, when they claimed that products were about as toxic as methyl parathion. They estimated environmental hazard from intravenous LD_{50} of 10 mg/kg for rats, which was reportedly listed in the Registry of Toxic Effects of Chemical Substances (4). (The Registry actually lists intravenous LD_{Lo} of 10 mg/kg for dogs.) However, intravenous toxicity is not a fair estimate for environmental toxicity. A better estimate is the oral LD_{50} of 350 mg/kg for rats (4). Since p-nitrophenol is significantly less hazardous than methyl parathion (oral LD_{50} for rats is 9 mg/kg), alkaline hydrolysis is suitable for chemical degradation.

Table 25. Summary of Hydrolysis Data for Methyl Parathion. Adapted from Shih and Dal Porto (1).

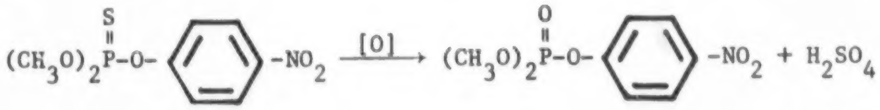
Solvent	Temperature	Hydrolysis Half-life
Water (pH 1-5)	20°C	$t_{\frac{1}{2}} = 175$ days
0.01N NaOH	30°C	$t_{\frac{1}{2}} = 210$ min.
1.0N NaOH	15°C	$t_{\frac{1}{2}} = 32$ min.
1N NaOH	20°C	$t_{\frac{1}{2}} = 4.4$ min.
1N NaOH/acetone (1:1)	20°C	$t_{\frac{1}{2}} = 10.7$ min.

Microencapsulation appears to have a minimal effect on the chemical hydrolysis of methyl parathion. The cell wall does not consume hydroxide at a rate competitive with the methyl parathion hydrolysis (51). Methyl parathion appears to leach rapidly and quantitatively from the micro-capsules. Karr evaluated recovery of methyl parathion by its extraction with acetonitrile from the microcapsules (52). When cell walls were destroyed by grinding the capsules the extraction recovered 100% of the methyl parathion. Without the grinding about 90-95% of methyl parathion was recovered. It is expected that 50% aqueous ethanol is also a suitable medium for extracting the methyl parathion in PennCap-M (51, 53).

Shih and Dal Porto discussed two other possibilities for methyl parathion detoxification (1): reduction of the nitro group to yield the non-toxic O,O-dimethyl O-*p*-aminophenyl thiophosphate

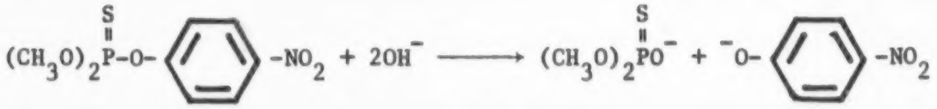


and oxidation to yield paraoxon:



Although they did not recommend either approach for detoxification, they did suggest further study of methyl parathion reduction to the corresponding amine as a possible method. The present study agrees with their conclusion that neither procedure is suitable for detoxification. The reduction requires a very corrosive acid (9:1 mixture of acetic and hydrochloric acid) and techniques which only a skilled chemist should attempt (54). Hsieh and coworkers have evaluated alkaline sodium hypochlorite on parathion degradation (53). They have found a significant increase in the degradation rate; their results are detailed in Appendix F. Since the oxidation yields the more toxic methyl paraoxon as an intermediate, it is not recommended.

Alkaline hydrolysis is proposed for decontaminating PennCap-M. Time for 99.9% degradation, $t_{0.999}$, was calculated by Equation (A-7), based upon a rate constant of 0.16 ℓ/mole-min. and a 2:1 hydroxide-methyl parathion stoichiometry:



About 8:1 (vol/vol) of 1N sodium hydroxide in 50% aqueous ethanol is suggested for PennCap-M (0.91 moles/ℓ of methyl parathion); $t_{0.999}$ was calculated about 75 minutes for these conditions. Additional time should be allotted to insure complete leaching of the methyl parathion from the microcapsules.

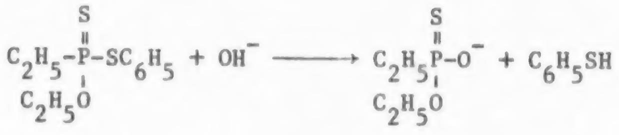
Alkaline rinse is suggested for empty containers (Section 3). Detoxification of methyl parathion in rinsate is discussed in Appendix F.

A.12 CHEMICAL METHODS FOR DETOXIFICATION OF DYFONATE

Dyfonate is an insecticide applied for control of soil pests affecting a wide variety of vegetables, grains, turf, sugarcane and sugarbeet, and tobacco. It is available as an emulsified concentrate (4 lbs/gal), granulars (5, 10, and 20% by weight), and dry bait (4% by weight). Dyfonate is miscible with organic solvents; its water solubility is 13 ppm (14, 15, 55).

Dyfonate reacts with peroxides to yield a variety of products. Although Stauffer Chemical Co. formerly recommended degradation with hypochlorite (2), they no longer suggest this treatment (56). Although complete oxidation will yield non-toxic products, partial oxidation will yield more toxic oxon intermediate products (8, 43, 57). Six products have been identified from oxidation by m-chloroperbenzoic acid. The major products are the corresponding phosphenyl phenyl disulfide (20% to 30% yield) and the corresponding oxon (about 20% yield); other products were phosphonic acid, phosphonothioic acid; sulfur, and diphenyl disulfide (43, 57). The oral LD_{50} for Dyfonate is 16 mg/kg while for the oxon it is 2.7 mg/kg (4).

Dyfonate hydrolyzes in aqueous base to yield the ethyl ester of ethyl phosphonothioic acid and phenyl mercaptan (58). The phosphonothioate monoester is expected to have low toxicity.



$$C_2H_5-\underset{C_2H_5O}{\overset{\overset{S}{\|}}{P}}-SC_6H_5 + OH^- \longrightarrow C_2H_5\underset{C_2H_5O}{\overset{\overset{S}{\|}}{P}}-O^- + C_6H_5SH$$

Phenyl mercaptan is toxic: oral LD_{50} of 46 mg/kg for rats (4). Phenyl mercaptan is readily converted with mild chemical oxidants to diphenyl disulfide, $(C_6H_5)_2S_2$ (48). Diphenyl disulfide appears much less toxic; the interperonital LD_{Lo} (for rats) is 100 mg/kg (4). Stronger oxidizing conditions convert phenyl mercaptan to benzene sulfonic acid (oral LD_{50} of 890 mg/kg for rats) (4, 48). Studies on the environmental fate for Dyfonate indicate that phenyl mercaptan is a fugitive in soil. It rapidly metabolizes to simple low hazard derivatives such as methyl phenyl sulfide (56).

Although alkaline hydrolysis appears to reduce the toxicity of Dyfonate, insufficient data are available to suggest a practical method. An alternative non-chemical method should be used for disposal; the EPA recommended procedures should be followed (7a). Empty containers should be thoroughly drained and triple-rinsed by the NACA recommended method (Section 3).

APPENDIX B.

CHEMICAL METHODS FOR THE DETOXIFICATION OF NITROGEN-CONTAINING PESTICIDES

B.1 GENERAL REVIEW OF APPLICABLE DISPOSAL METHODS

The nitrogen-containing pesticides encompass a broader range of commercial applications, toxicological properties, and physical and chemical behavior than seen in the organophosphate pesticides. The variety of uses include insecticides, herbicides, fungicides, plant growth regulators and fumigants. Table 26 presents the selected nitrogen-containing pesticides and their structures. These pesticides represent twelve subdivisions based upon chemical structure. For facilitation of general discussion these pesticides can be designated either as carbonyl (or carbamoyl) $\overset{X}{\overset{\|}{-C-}}$ where X is oxygen or sulfur, or "other." The first group includes carbamates, thiocarbamates, dithiocarbamates, anilides, imides and hydrazides, amides, and ureas and uracils. All of these can be hydrolyzed. Their kinetic behavior follows the same scheme as the phosphates (Equations A2-11). Unlike the phosphates the hydrolysis does not almost always affect toxicity. Only the carbamates as a class are acetylcholinesterase inhibitors which can be detoxified by hydrolysis. The "other" group of nitrogen-containing pesticides encompasses the amines (including the triazenes, heterocyclic amines, and quarternary ammonium compounds), the nitro-compounds and miscellaneous group.

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Table 26. Chemical Structures of Selected Nitrogen-Containing Pesticides

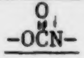
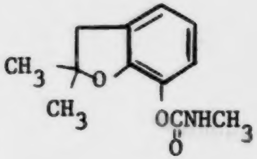
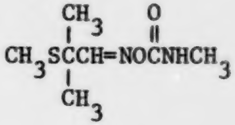
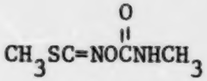
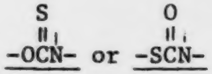
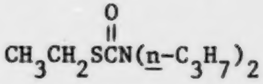
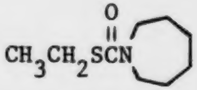
Class	Pesticide Name Common	 Trade	Structure	Molecular Weight (g)
Carbamates			 $\underline{-O\overset{O}{\overset{\parallel}{C}}N-}$	
	Carbofuran	Furadan		221.3
	Aldicarb	Temik	 $CH_3S\overset{CH_3}{\underset{CH_3}{C}}CH{=}NO\overset{O}{\overset{\parallel}{C}}NHCH_3$	190.3
	Methomyl	Lannate, Nudrin	 $CH_3SC{=}NO\overset{O}{\overset{\parallel}{C}}NHCH_3$	162.2
Thiocarbamates			 $\underline{-O\overset{S}{\overset{\parallel}{C}}N-}$ or $\underline{-S\overset{O}{\overset{\parallel}{C}}N-}$	
	EPTC	Eptam	 $CH_3CH_2S\overset{O}{\overset{\parallel}{C}}N(\underline{n}-C_3H_7)_2$	189.3
	Molinate	Ordram		187.3

Table 26. Chemical Structures of Selected Nitrogen-Containing Pesticides (Cont'd.)

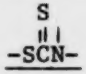
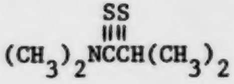
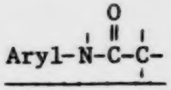
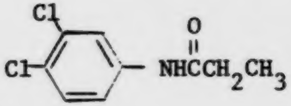
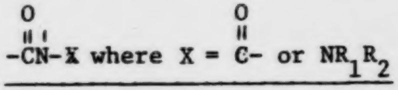
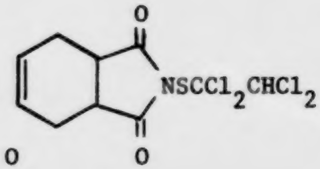
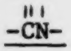
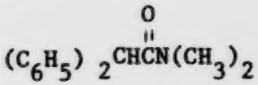
Class	Pesticide Name Common	 Trade	Structure	Molecular Weight (g)
Dithiocarbamates			 $\underline{-S\overset{S}{\overset{\|}{C}}N-}$	
	Thiram		 $(CH_3)_2N\overset{S}{\overset{\|}{C}}\overset{S}{\overset{\|}{C}}H(CH_3)_2$	240.4
Anilides			 $\underline{\text{Aryl}-N-\overset{O}{\overset{\|}{C}}-C-}$	
	Propanil			218.1
Imides and Hydrazides			 $\underline{-\overset{O}{\overset{\|}{C}}N-X \text{ where } X = \overset{O}{\overset{\|}{C}}- \text{ or } NR_1R_2}$	
	Captafol			349.1
Amides			 $\underline{-\overset{O}{\overset{\|}{C}}N-}$	
	Diphenamid		 $(C_6H_5)_2CH\overset{O}{\overset{\|}{C}}N(CH_3)_2$	239.3

Table 26. Chemical Structures of Selected Nitrogen-Containing Pesticides (Cont'd.)

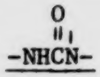
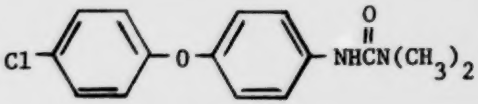
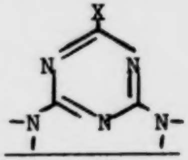
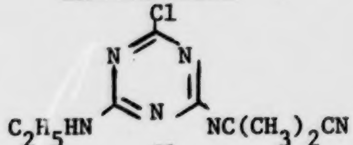
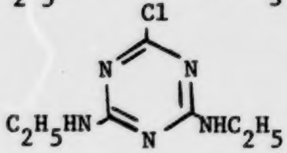
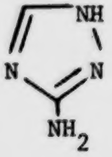
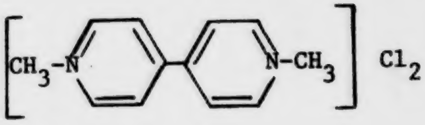
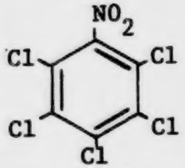
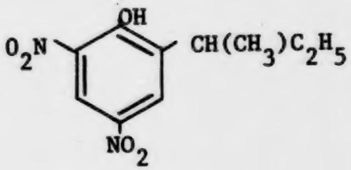
Class	Pesticide Name Common	 Trade	Structure	Molecular Weight (g)
Ureas and Uracils			 $-NH\overset{O}{\overset{\|}{C}}N-$	
	Chloroxuron			290.7
Triazenes				
	Cyanazine	Bladex		240.7
	Simazine			201.7
Heterocyclic Amines				
	Aminotriazole	Amitrole		84.1

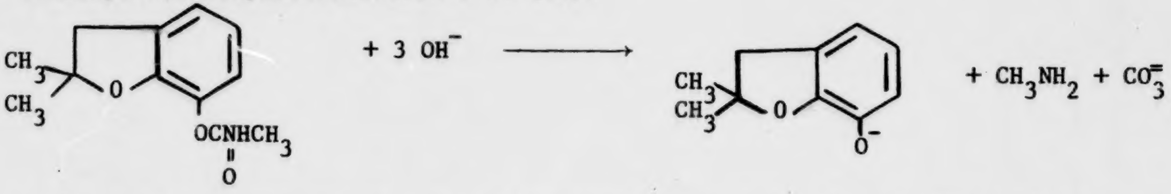
Table 26. Chemical Structures of Selected Nitrogen-Containing Pesticides (Cont'd.)

Class	Pesticide Name Common	 Trade	Structure	Molecular Weight (g)
Quaternary Ammonium Compounds				
	Paraquat (as Paraquat dichloride)			186.3 (257.2)
Aromatic Nitro Compounds				
	PCNB	Terrachlor		295.4
	Dinoseb			240.2
Other Nitrogen-Containing Compounds				
	Chloropicrin		Cl_3CNO_2	164.4

B.2 CHEMICAL METHODS FOR DETOXIFICATION OF CARBOFURAN

Carbofuran (Furadan) is a broad band insecticide, miticide and nematocide, which is applied to field crops, grains, cotton and tobacco. Solubility is 700 ppm in water, 4% (W/W) in ethanol and in benzene, and 15% in acetone. It is available as a 4 lb/gal flowable and granule (2, 3, 5 and 10%) (14, 16, 59).

The chemical behavior of carbofuran is analogous to carbaryl, which Shih and Dal Porto reviewed (1). While carbofuran is relatively stable in acid and neutral media, it hydrolyzes in alkali to yield methylamine, carbonate, and 2,2-dimethyl-2,3-dihydrobenzofuran-7-ol (60).



Carbonate is non-toxic and methylamine has subcutaneous LD_{Lo} of 2500 mg/kg for mice (4). The benzofuranol appears stable in strong alkali. No information was available on its toxicity, its environmental fate, or the toxicity of its metabolites. Metabolic studies of carbofuran suggest that the benzofuranol might be oxidized to 3-hydroxy- and 3-keto-derivatives (60, 61). Although the toxicities of the benzofuranol and its potential metabolites are not known, they are expected to be on the same order as α-naphthol, which is the hydrolysis product of carbaryl (1).

Metcalf and coworkers studied hydrolysis kinetics for 0.1% (w/v) carbofuran in methanol in a pH 9.5 buffer (62). The pseudo first-order rate constant was $1.04\text{x}10^{-2}\text{min}^{-1}$ which yields a bimolecular rate constant of $3.35\text{x}10^{3}$ ℓ/mole-min (from Equation A-11). The rate constant for 25°C was calculated by the Arrhenius relationship (Equation A-9) assuming that the activation energy,

E_A = 20 kcal/mole, is about the same for alkaline hydrolysis of carbofuran and carbaryl (1). This yielded a bimolecular rate constant of 170 ℓ/mole-min. This value is similar to the rate constant for 340 ℓ/mole-min for carbaryl hydrolysis at 25°C (1), which is expected since the two have similar chemical structures.

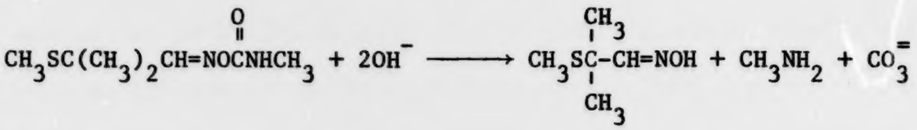
A decontaminant solution of sodium hydroxide in 50% aqueous ethanol is recommended to achieve sufficient carbofuran dissolution. $t_{0.999}$, 99.9% degradation time was calculated by Equation A-7 with n = 3 (3:1 hydroxide-carbofuran stoichiometry). For the 4 lb/gal flowable formulation $t_{0.999}$ was calculated as less than 1 minute with 20:1 (v/v) 1N NaOH or 10:1 (v/v) 2N NaOH. Additional time is suggested for granular formulations to allow the carbofuran to desorb. The 10%, 5%, and 2% formulations (0.2, 0.1, and 0.05 moles/lb, respectively), can also be detoxified with 1N NaOH in 50% aqueous ethanol.

Bags should be thoroughly emptied and disposed according to the EPA recommended procedures (7a). Empty containers should be drained thoroughly and triple rinsed with the aqueous ethanolic alkaline decontaminant or water, if the rinsate could be used for dilution (Section 3).

B.3 CHEMICAL METHODS FOR DETOXIFICATION OF ALDICARB

Aldicarb is a systemic, soil applied insecticide. Because of its very high acute toxicity, it is only marketed as a granular formulation. It is available as 5, 10, or 15% active ingredients and in 10 and 25 lb bags. Aldicarb is applied to a broad range of crops and ornamentals (14, 63). It is soluble in chlorinated hydrocarbons, ketones and aromatic hydrocarbons. Water solubility is 6 g/ℓ at 30°C. Aldicarb can rapidly be oxidized to its sulfoxide and then more slowly to the sulfone. The sulfoxide is very water soluble (more than 33%) (15).

Aldicarb's hydrolysis behavior is typical for carbamates. It is stable in neutral media, but hydrolyzes in acid and base. It is most rapidly hydrolyzed by base (60, 63). Alkaline hydrolysis yields β-methyl-β-thiomethylpropionaldehyde oxime, methylamine, and carbonate (64, 65):



$$CH_3SC(CH_3)_2CH{=}NO\overset{O}{\overset{\|}{C}}NHCH_3 + 2OH^- \longrightarrow CH_3S\underset{CH_3}{\overset{CH_3}{C}}{-}CH{=}NOH + CH_3NH_2 + CO_3^{=}$$

The oxime appears to be relatively stable in base. A minor component of the alkaline hydrolysis is the dehydration product, the corresponding nitrile (66). The oxime is hydrolyzed in acidic media to yield the aldehyde and hydroxylamine (64, 65).

$$CH_3SC(CH_3)_2CH{=}NOH + H_2O \xrightarrow{H^+} CH_3SC(CH_3)_2CHO + NH_2OH$$

The hydrolysis products have a lower acute hazard than aldicarb. Methylamine has a relatively low hazard. Oral LD_{50} (rats) for the oxime is 0.77 ml/kg

(66). No information was available for the corresponding aldehyde. Since the oxime's acute toxicity is low, it is reasonable to expect that the aldehyde toxicity is also low. Since hydroxylamine and some of its derivatives are suspected mutagens (67), the oxime is also suspect. Hydrolysis of the oxime to yield the aldehyde is a better procedure, but it would require greater technical skills and time commitment than could be expected of the layman.

Oxidants such as peracidic acid convert the sulfur group in aldicarb to the corresponding sulfoxide and sulfone (60, 68). The oxidation does not significantly alter toxicity: oral LD_{50} for rats is 0.9 and 25 mg/kg for the sulfoxide and sulfone, respectively. The hydrolysis is faster for the oxidized analogs. Comparative hydrolysis data are summarized in Table 27. Metabolic oxidation also produces the sulfoxide and sulfone (61, 63).

Table 27. Half-lives for Aldicarb and Oxidized Derivative Hydrolysis in Water (69)

		Half-life (minutes)	
Product	pH	80°C	110°C
Aldicarb	6	1140	115
	7	205	54
	8	49	7
Aldicarb sulfoxide	6	80	20
	7	45	8
	8	3	0.5
Aldicarb sulfone	6	120	50
	7	15	< 1
	8	1.5	< 0.5

The time for 99.9% degradation was calculated with Equation (A-7) with a rate constant, k, of $1.2\text{x}10^{-2}$ ℓ/mole-min. for aldicarb hydrolysis in 50% aqueous ethanol at ambient temperature (63). The stoichiometry of the alkaline hydrolysis requires a minimum hydroxide-aldicarb of 2:1; additional base might be consumed by the oxime, which is a weak acid (48):

$$CH_3SC(CH_3)_2CH{=}NOH + OH^- \rightleftharpoons CH_3SC(CH_3)_2CH{=}NO^- + H_2O$$

Table 28 summarizes results and compares $t_{0.999}$ for the various formulations hydrolyzed by 1N and 2N hydroxide. Better hydrolysis times were obtained for 2N NaOH decontaminant solutions, and it is recommended for use. Since the pesticide must dissolve in order to be hydrolyzed in the calculated time, overnight contact is suggested to allow for desorption.

Bags should be thoroughly emptied before disposal. They should be disposed by the EPA recommended procedures (Section 3) (7a).

Table 28. Calculated Time for 99.9% Degradation of Aldicarb in 50% Aqueous Ethanol at Ambient Temperature

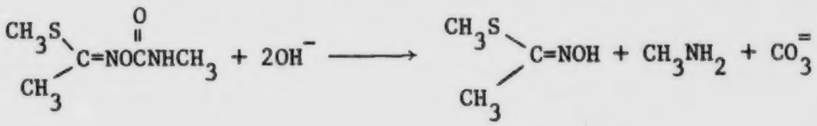
Formulation	Aldicarb (moles/lb)	$t_{0.999}$ n = 2	$t_{0.999}$ n = 3
15%	0.36	13.9[a]	18.5[a]
		5.7[b]	6.3[b]
		5.2[c]	5.4[c]
10%	0.24	11.8[a]	13.9[a]
		5.4[b]	5.7[b]
5%	0.12	10.7[a]	11.3[a]
		5.1[b]	5.2[b]

(a) 2 liters of 1N NaOH/pound granular formulation
(b) 2 liters of 2N NaOH/pound granular formulation
(c) 4 liters of 1N NaOH/pound granular formulation

B.4 CHEMICAL METHODS FOR DETOXIFICATION OF METHOMYL

Methomyl (Lannate, Nudrin) is applied for insects and nematodes control in a broad range of vegetables, fruits, field crops and ornamentals. It is formulated as a 90% water soluble powder, 24% emulsifiable concentrate (1.8 lbs/gal), and 2% and 5% dust. Methomyl is water soluble (58 g/ℓ) and is very soluble in alcohols and aromatic solvents (14, 15, 70).

Methomyl's chemical reactivity is similar in some respects to aldicarb (Appendix B.3). Its hydrolysis parallels aldicarb, but it appears more resistant to oxidation (71). Methomyl hydrolysis is fastest in alkaline media (60). Alkaline hydrolysis products are dimethylamine, carbonate and methyl-N-hydroxythioacetimidate (72).



$$\mathrm{(CH_3S)(CH_3)C{=}NOC(=O)NHCH_3 + 2OH^- \longrightarrow (CH_3S)(CH_3)C{=}NOH + CH_3NH_2 + CO_3^{=}}$$

The oxime appears resistant to hydrolysis. Carbonate and methylamine are nontoxic (4). The oxime has a lower acute toxicity than methomyl, which is an acetylcholinesterase inhibitor (71). Oximes as a class are suspected carcinogens (67). Feeding studies with rats have shown no apparent chronic effects for methomyl (72). Since the oxime is a methomyl metabolite, the oxime is also expected to show no chronic effect (72, 73).

Relatively little information was found to describe kinetics. The only useable data was a report on methomyl degradation at aqueous pH 9.1, Table 29. Details of the study were not available (70, 71).

Table 29. Degradation of Methomyl in Water at pH 9.1 (70).

Time in Solution	Percent Methomyl Loss	
	8 oz/100 gal	16 oz/100 gal
0	0	0
4 hrs	4	3
6 hrs	5	3
24 hrs	11	8
2 days	18	13
3 days	22	18
6 days	39	30

A rate constant was calculated for 39% degradation at 6 days and assuming that the hydrolysis was pseudo-first order (hydroxide concentration remains constant). Using Equations (A-6 and 11) the rate constant, k, was calculated as 4.17 ℓ/mole-hour. This is about two orders of magnitude faster than for aldicarb. Time for 99.9% degradation, $t_{0.999}$, was calculated from Equation (A-7). Stoichiometry for methomyl hydrolysis is the same as for aldicarb; n is expected to be slightly above 2.

Since methomyl is relatively water soluble, aqueous 2N sodium hydroxide is considered a suitable decontaminant. $t_{0.999}$, 99% degradation time, was calculated as 1.4 hours for the flowable formulation with 5:1 (v/v) ratio of decontaminant to pesticide; 1.3 hours for the 90% soluble powder with 3.7ℓ decontaminant per pound; and 1.2 hours or less for the 2% and 5% dusts with 1ℓ decontaminant per pound.

Empty containers should be thoroughly drained and then rinsed with an alkaline decontaminant or water if the rinsate could be used for dilution. Bags should be thoroughly emptied and then disposed as the EPA has recommended (Section 3).

B.5 CHEMICAL METHODS FOR DETOXIFICATION OF EPTC

EPTC (Eptam) is a preemergent herbicide used to control annual and perennial weeds for numerous field crops. It is primarily marketed as a 7 lb/gal emulsifiable concentrate. Eptam is miscible in all proportions with acetone, methanol and aromatic solvents, and soluble in most organic solvents. Aqueous solubility is 365 ppm at 20°C (14, 75, 76). Eptam has a low toxicity for rats and mice (oral LD_{50} of 1630 and 750, respectively) but is moderately toxic for cats (112 mg/kg) (4).

EPTC can be hydrolyzed to di-*n*-propylamine, ethyl mercaptan and CO_2 (or carbonate) (45, 76). The hydrolysis products are more toxic to rats than EPTC; oral LD_{50} values are 930 and 682 mg/kg for di-*n*-propylamine and ethyl mercaptan, respectively (4). EPTC does have moderate aquatic toxicity (Table 6); no information on aquatic toxicities of the hydrolysis products was found. EPTC hydrolysis is very slow in dilute acid or base. Less than 5% hydrolyzed after 300 days at 20°C in 0.1N H_2SO_4, HCl or NaOH. It hydrolyzes completely after heating at 85°C for 10 minutes in 96% sulfuric acid (45). This strong acid is only suitable for use by trained personnel.

EPTC can be oxidized to yield di-*n*-propylamine and ethanesulfonic acid (28). Di-*n*-propylamine (oral LD_{50} of 930 mg/kg for rats) is non-toxic. No toxicity information was found for ethanesulfonic acid (4). The reaction conditions and degradation times were not available.

Since no acceptable chemical detoxification is available, EPTC should be disposed by the EPA recommended, alternative procedures (7a). Empty containers should be thoroughly drained then disposed by the EPA recommended procedures (Section 3).

B.6 CHEMICAL METHODS FOR DETOXIFICATION OF MOLINATE

Molinate is a selective herbicide for broadleaved and grassy weeds. It is recommended for control of watergrass in rice. It is soluble at 800 ppm in water, but is miscible in all proportions with kerosene, ketones, xylene and toluene. It is formulated as 10% granules and an 8 lb/gal emulsifiable concentrate (14, 15, 78).

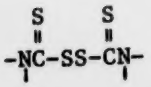
Molinate is relatively resistant to hydrolysis. It will hydrolyze in strong acid (96% sulfuric acid) to yield hexamethylenimine (hexahydro-1H azepine) (18). Hexamethylenimine, which has an oral LD_{50} of 33 mg/kg for rats, is more toxic than molinate (oral LD_{50} of 501 mg/kg for rats) (4). No other information was found for the chemistry of molinate.

Molinate should be disposed by a non-chemical, alternative method as recommended by the EPA (7a). Bags should be thoroughly emptied and bottles and drums should be thoroughly drained and triple rinsed by the NACA recommended procedure (Section 3).

B.7 CHEMICAL METHODS FOR DETOXIFICATION OF THIRAM

Thiram is applied as a seed treatment and a fungicide for turf, shrubs and ornamentals, fruit trees, and vegetables. Thiram solubility is low in water (30 ppm) and relatively low in methanol and ethanol (<1 g/100 ml). It is slightly soluble in carbon tetrachloride and xylene; moderately soluble in benzene, dioxane, and ketones; and soluble (230 g/ℓ) in chloroform. Thiram is formulated in a wide variety of products, often in combination with other pesticides. Formulations include dusts and wettable powders containing 50 to 75% active ingredients and 42% liquid suspension (4 lb/gal) (14, 15, 79).

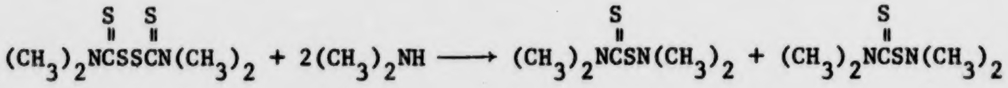
Thiram is a member of the thiuram family, whose common structural unit is disulfide bonded to carbamoyl groups.



$$-\underset{|}{\mathrm{N}}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{-SS-}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\underset{|}{\mathrm{N}}-$$

The thiuram structure reacts by redox (oxidation-reduction) and ionic mechanisms. Its chemistry has been extensively reviewed by Thorn and Ludwig (80).

When thiram is refluxed with acetic acid or acetic anhydride, it yields CS_2, COS, and dimethylamine. Several products are formed when thiram is refluxed with acetone; those identified include dimethylamine, CS_2, and three products of dimethylcarbomyl bonded to acetone. Thiram reacts with cyanide ion to yield the monosulfide and thiocyanate. Thiram reacts with dimethylamine in benzene at 50° to form an ammonium salt and sulfenamide; product toxicity is unknown.



$$(\mathrm{CH_3})_2\mathrm{N}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SS}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{N}(\mathrm{CH_3})_2 + 2(\mathrm{CH_3})_2\mathrm{NH} \longrightarrow (\mathrm{CH_3})_2\mathrm{N}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SN}(\mathrm{CH_3})_2 + (\mathrm{CH_3})_2\mathrm{N}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SN}(\mathrm{CH_3})_2$$

Thiram is reduced by several metals and metal complexes, including zinc, copper and Cu(I) salts, to yield metal salts of dimethyldithiocarbamic acid. Although these salts have low oral toxicities, some of these salts also have shown positive carcinogenic effects, for example, the zinc salt (Ziram) (4). Acid treatment of these salts degrades them and yields carbon disulfide and dimethylamine (80, 81). Other reducing agents, such as sulfide and bisulfite also cleave the thiuram disulfide; treatment with H_2S can directly reduce thiram to dimethylamine and carbon disulfide.

Thiram reduction is not suitable for general use. Dimethylamine is slightly toxic (oral LD_{50} = 698 mg/kg for rats). Although carbon disulfide has a relatively low acute toxicity, it is a relatively low boiling material (46.1°C) with a strong, disagreeable odor and is inflammable (38). Because thiram has a relatively low solubility in water, alcohol, or ketones, the reduction will require either reflux with these solvents or use of chloroform or a comparable organic solvent. The reagents and reaction conditions require technical skills too advanced for general use.

Waste thiram should be disposed as described by the EPA (7a). Bags should be thoroughly emptied before disposal. Empty bottles and drums should be thoroughly drained and triple rinsed by the NACA recommended method (Section 3).

B.8 CHEMICAL METHODS FOR DETOXIFICATION OF PROPANIL

Propanil is applied as a post-emergent herbicide to control grasses and weeds. It is formulated as a 35% emulsifiable concentrate (3 lb/gal) (15, 82, 83). It has a low water solubility (20 mg/100 ml) and is very soluble in methanol, benzene, and acetone (15, 45).

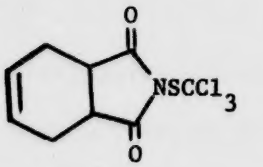
Propanil is hydrolyzed by acid or base to yield propanoic acid and 3,4-dichloroaniline (15, 45). 3,4-Dichloroaniline (oral LD_{50} = 648 mg/kg) is only slightly less toxic to rats than propanil (oral LD_{50} = 560 mg/kg) (4). Soil microorganisms metabolize propanil to 2,4-dichloroaniline which further metabolizes to chloroazobenzene. Products are very persistent in the soil (84).

Propanil should be disposed by a non-chemical alternative as described by the EPA (7a). Rohm and Haas suggest diluting propanil with a flammable solvent and incineration (82). Empty containers should be thoroughly drained and triple rinsed by the NACA recommended method (Section 3).

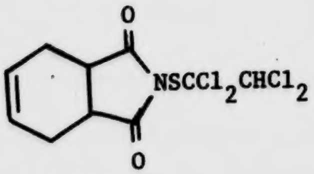
B.9 CHEMICAL METHODS FOR DETOXIFICATION OF CAPTAFOL

Captafol (Difoltan) is a broad spectrum fungicide for control of economic diseases of fruits, vegetables, ornamentals, and turf grasses. It is also applied for seed and soil treatment (14, 15, 85). Captafol is available as an 80% wettable powder, a 4 lb/gal flowable and in several formulations for seed treatment. Captafol is practically water insoluble (1.4 ppm), moderately soluble in acetone (4.3 g/100 ml) and slightly soluble in alcohols (18, 85).

Captafol is similar in physical and chemical properties to the fungicide captan, which Shih and Dal Porto reviewed (1). They recommended alkaline detoxification:



Captan



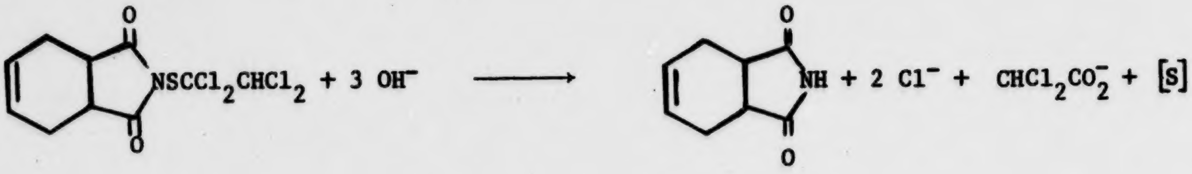
Captafol

Captafol is relatively stable in acid and neutral conditions, but hydrolyzes rapidly in alkali (15, 18, 86). Wolfe and coworkers have compared hydrolysis rates of captan and captafol. At 28°C pseudo-first order rate constants were 6.5×10^{-5} sec^{-1} (pH 7.07) and 7.07×10^{-5} sec^{-1} (pH 7.17), respectively (87). Equation (B-1) describes the pH dependence of the pseudo-first order rate constant k, in buffer:

$$k = k_{H_2O} + k_{OH^-}C_{OH^-} \qquad \text{B-1}$$

This expression is expected for the alkaline region of Equation (A-2). A rate constant for alkaline hydrolysis of captafol was estimated by assuming that captafol and captan have similar rate constants at all alkaline pH and that the water hydrolysis rate, k_{H_2O}, is small. Since captan hydrolysis rate is 1.1×10^{-3} sec^{-1} at pH 8.25 and 28°C, the second-order rate for captafol is estimated as 1.17×10^4 ℓ/mole-min.

The hydrolysis stoichiometry is not certain. Captafol is hydrolyzed by alkali to tetrahydrophthalimide, hydrogen chloride, dichloroacetic acid and various oxidation states of sulfur (28, 86, 87).



The minimum hydroxide captafol ratio necessary for complete hydrolysis is 3. However, additional demands for hydroxide can result in a higher value. Although the imide and dichloroacetic acid can hydrolyze further to ultimately yield ammonia and cyclohex-2-ene-1,2-dicarboxylic acid, rates are slow and it is not a practical concern (86). However, the imide which is a weak acid (48) and any sulfur present as hydrogen sulfide will require hydroxide for neutralization. To insure sufficient hydroxide for hydrolysis, a minimum ratio 10:1 hydroxide to captafol is recommended. Time for 99.9% degradation, $t_{0.999}$, was calculated with Equation (A-7). $t_{0.999}$ is less than 1 minute with a 10:1 molar excess of base, even with n as high as 6.

The hydrolysis products are not fungicidally active (1). Sodium chloroacetate (intravenous LD_{50} = 1880 mg/kg for mice), chloride, and carbonate are non-toxic (4). Sulfides are moderately toxic but are not considered a serious hazard in alkaline media (38). Tetrahydrophthalidimide is not an acute toxicant, but it has shown teratogenic effects with hamsters (4). Empty containers should be thoroughly drained before disposal. Empty bottles and drums should be thoroughly drained and rinsed (Section 3). Empty bags should be disposed as recommended by the EPA (7a).

B.10 CHEMICAL METHODS FOR DETOXIFICATION OF DIPHENAMID

Diphenamid is a selective pre-emergence herbicide for control of annual grasses and broadleaf weeds in field crops, fruit shrubs and trees, ornamentals and lawns. It has a low water solubility (260 ppm at 25°C) but is soluble in acetone and xylene. It is formulated as 50% and 80% wettable powder, 5% granule and, 4 lb/gal liquid dispersant (14, 15).

The Diphenamid toxicity reported in the Registry of Toxic Effects of Chemical Substances (oral LD_{50} of 293 mg/kg for rats) might overstate the hazard (4, 88). This value was derived in a study with newborn rats. The Upjohn Company used adult rats in toxicity tests and obtained an oral LD_{50} greater than 1000 mg/kg (88).

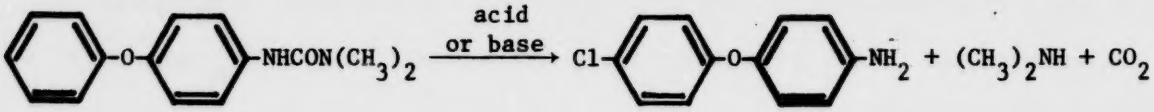
Diphenamid is relatively resistant to hydrolysis by acid or base. Holden and coworkers evaluated hydrolysis in 0.5N potassium hydroxide at 40°C (89). The hydrolysis products are diphenylacetic acid and dimethylamine. They detected less than 4% dimethylamine after 30 minutes. Although the hydrolysis products are less phytotoxic, the hydrolysis is too slow for practical use.

Small quantities of Diphenamid can be disposed by the EPA recommended procedures as an alternative to chemical detoxification. Sacks should be thoroughly emptied then disposed by the EPA recommended procedures. Empty bottles and drums should be thoroughly drained and triple rinsed by the NACA recommended method (Section 3) (7a).

B.11 CHEMICAL METHODS FOR DETOXIFICATION OF CHLOROXURON

Chloroxuron (Tenoran) is a herbicide used primarily as a post-emergence herbicide for annual broadleafs and also a small use as a pre-emergent herbicide. It has a low water solubility (3.7 ppm at 20°C), is slightly soluble in alcohol, and is very soluble in acetone. It is formulated as a 50% wettable powder and 5% granular (15, 90).

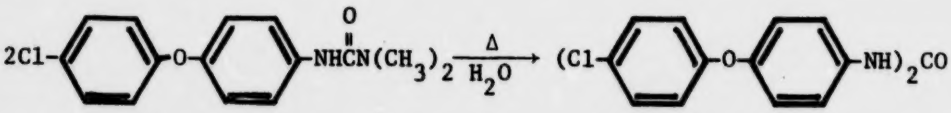
Chloroxuron is hydrolyzed by strong acids or bases to p-(p-chlorophenoxyl) aniline, dimethylamine and carbon dioxide (90):



Although aqueous hydrolysis rates were not given for chloroxuron, based upon information available for hydrolysis of other area pesticides its hydrolysis rate is expected to be slow. Carbon dioxide is non-toxic and dimethylamine is slightly toxic (oral LD_{50} = 698 mg/kg for rats) (4).

The toxicity of the aniline was not found by literature search. Since several anilines are carcinogenic, the p-(p-chlorophenoxy) aniline is also suspect (4, 67).

A few other reactions of the ureas are known, but none of them are practical disposal methods. Heating chloroxuron in water results in cross-amination (90).

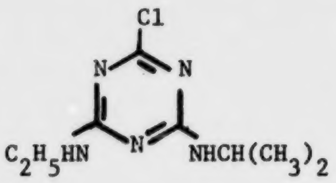


Chloroxuron must be disposed by alternative, non-chemical procedures as recommended by the EPA (7a). Bags should be thoroughly emptied and disposed by the EPA recommended procedures (Section 3) (7a).

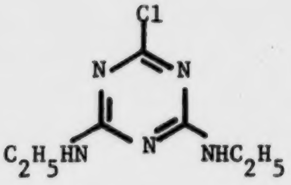
B.12 CHEMICAL METHODS FOR DETOXIFICATION OF SIMAZINE

Simazine (Princep) is a selective and broad band pre-emergent herbicide. Its solubility is low in water (5 ppm), methanol (400 ppm) and chloroform (900 ppm). Its formulations include 50% and 80% wettable powder, and 4% and 8% granules (15, 45).

Simazine has the characteristic physical and chemical properties of the s-triazene herbicides. This group has been extensively reviewed (90, 92); also Shih and Dal Porto (1) reviewed the analogous atrazine.

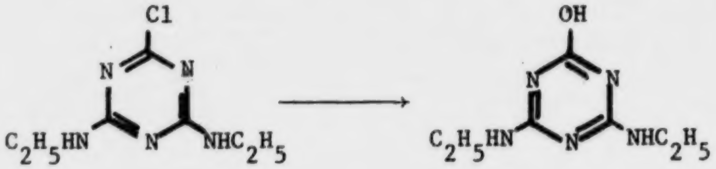


Atrazine



Simazine

Simazine is relatively non-toxic but is environmentally persistent. It is metabolized in soil to hydroxysimazine, which is not herbicidally active.



Simazine, like other s-triazenes, can be chemically hydrolized. Shih and Dal Porto (1) adopted a chemical hydrolysis procedure for atrazine detoxification.

The kinetic behavior of the s-triazenes parallel the organophosphates and carbamate pesticides (90, 92). Hydrolysis rate follows a bell-shaped pH profile. The rate is slowest in the central pH range and most rapid at pH extremes. Kinetic arguments in Appendix A can be applied to the s-triazenes (93). The kinetic scheme requires homogeneous solution of pesticide. Shih and Dal Porto calculated the 99.9% degradation time, $t_{0.999}$, for atrazine hydrolysis at ambient temperature and pH 14 (1). However, since a number of their assumptions were wrong, their estimated $t_{0.999}$ of 4.5 hours underestimates the required degradation time. Perhaps the most serious error was that the hydrolysis scheme uses an atrazine concentration very much higher than its aqueous solubility (93). There is no way to calculate the actual time required.

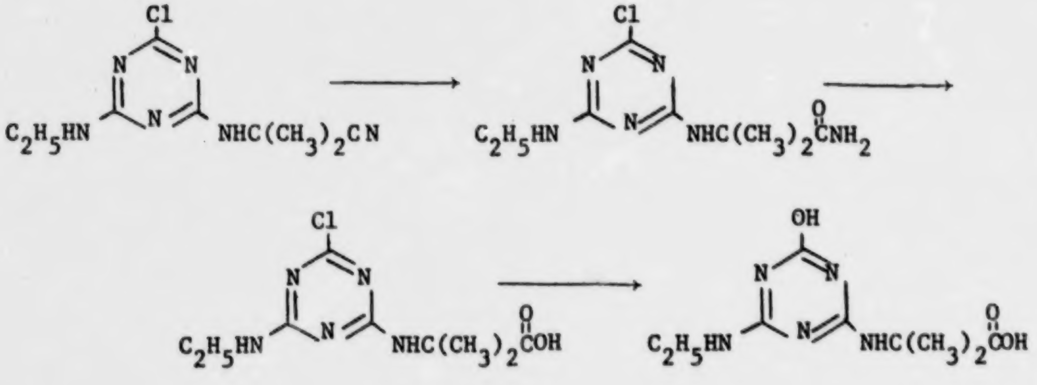
Simazine should be disposed by a non-chemical alternative as described in the EPA recommendations (7a). Empty containers should also be disposed by these recommendations (Section 3).

If simazine is to be disposed by land burial, mixture with lime (calcium hydroxide) could facilitate degradation. s-triazines are chemically hydrolyzed by acid or base at rates which are soil catalyzed (94). Lime is preferred to a strong acid, since it is solid, and relatively easy to handle.

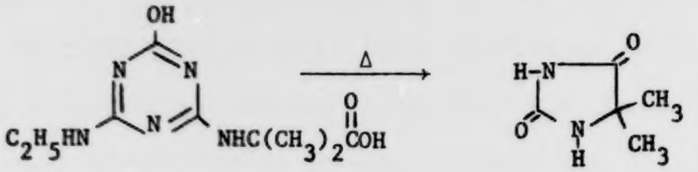
B.13 CHEMICAL METHODS FOR DETOXIFICATION OF CYANAZINE

Cyanazine (Bladex) is a pre- and post-emergence herbicide used for broad-leaved weeds and annual grasses. It has a low water solubility (191 ppm) and is ethanol soluble (45 g/ℓ). It is formulated as a 4 lb/gal water dispersible suspension, 80% wettable powder and 15% granule (14, 15).

Cyanazine's oral toxicity (LD_{50} = 340 mg/kg for rats) is more hazardous than for other triazenes which have oral LD_{50} values of 1000 mg/kg or more (2). This higher toxicity apparently results from the cyanide group, so it was anticipated that hydrolysis would reduce oral toxicity. However, information concerning chemical hydrolysis and toxicity of hydrolysis products is restricted as proprietary information (95). Lau and coworkers have reported that cyanazine is metabolized in soil by a series of hydrolyses (96). It is expected that chemical hydrolysis parallels metabolic hydrolysis by yielding identical intermediate products in a series of hydrolysis steps.



The hydroxy acid derivative can be further degraded to 5,5-dimethylhydantoin by heating it with a mixture of ferricyanide and sodium acetate in glacial acetic acid.


OH
N
N
N
C_2H_5HN
$NHC(CH_3)_2\overset{O}{\overset{||}{C}}OH$
Δ
H-N
O
CH_3
CH_3
O
N
H

Cyanazine should be disposed by an EPA recommended procedure (7a). Empty bottles and drums should be rinsed by NACA recommended procedures (Section 3).

B.14 CHEMICAL METHODS FOR DETOXIFICATION OF AMITROLE

Amitrole (3-amino-s-triazole) is a non-selective systemic herbicide used to control grasses and broadleaf weeds, poison ivy, and aquatic weeds; it is not applied to crops (14, 15). It is formulated as a 50% soluble powder and a 2 lb/gal liquid (97). Amitrole is highly water soluble (28 g/100 g at 23°C), less soluble in ethanol, and insoluble in nonpolar solvents (14, 15).

Amitrole exhibits the chemical behavior of an aromatic amine (98). It is stable toward hydrolysis and oxidation. The amine group ($-NH_2$) forms salts with acids, Schiff bases with aldehydes and ketones, amides from acyl chlorides and anhydrides, diazonium salts, and metal complexes. Product toxicities were not found. The triazole ring could be opened through reactions with methyl iodide. None of these reactions are practical detoxification approaches.

Amitrole is relatively non-persistent; half-lives are reported at 1.0 and 1.5 month at 30° and 15°C, respectively (92). However, it is transported very quickly with ground water (99).

Amitrole should be disposed by an EPA recommended alternative to chemical detoxification (7a). It is sold in cardboard containers (soluble powder) and 5 gallon plastic bottles (liquid). The empty bottles should be triple rinsed by the NACA recommended method. Cardboard containers should be disposed by an EPA recommended method (Section 3).

B.15 CHEMICAL METHODS FOR DETOXIFICATION OF PARAQUAT

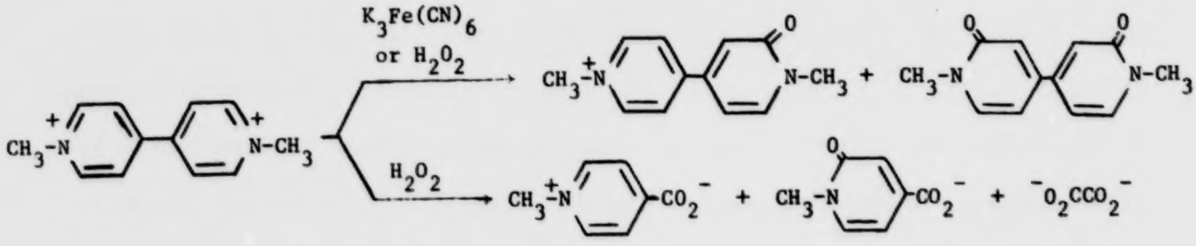
Paraquat is a quick acting herbicide and dessicant for weed and grass eradication before seeding; for weed control in orchards, shade trees and ornamentals; for industrial and roadside vegetation control; and for desiccation and defoliation of cotton. Paraquat is formulated as a 2 lb/gal soluble concentrate (15, 100).

Paraquat is the 1,1'-dimethyl-4,4'-bipyridinium dication. It is most commonly marketed as the dichloride salt but sometimes is available with other anions, such as methylsulfate. The anion is neither important for paraquat activity nor its detoxification. Paraquat is water soluble and slightly soluble in low-molecular weight alcohols (18, 100).

While paraquat is stable in acid and neutral media, it is hydrolyzed by base to yield an ill-defined resinous product (18). It was reportedly not affected by 100% methanolamine but was degraded by metallic sodium or lithium in liquid ammonia (99.9%) or sodium biphenyl (95%) (100a). Paraquat hydrolysis reportedly requires pH greater than 12 (100b). No information is available on the product composition or toxicity. Lawless and coworkers suggest hydrolysis with household detergent and burial of the product in clay soil for disposal (2). Because product fate in soil as well as product toxicity is unknown, the present study does not recommend paraquat hydrolysis for detoxification.

Paraquat reacts by chemical oxidation and reduction. With weak reducing systems it forms a stable free radical which can be reoxidized to paraquat with atmospheric oxygen. Strong reducing systems reduce it to 1-methylpiperidine (18).

Several oxidants will degrade paraquat. Calderbank (101) has described its oxidation by alkaline ferricyanide and by hydrogen peroxide. The milder oxidant, ferricyanide, yields the monopyridone and dipyridone. Oxidation with hydrogen peroxide yields these same products as well as the 4-carboxy-1-methylpyridinium ion. The pyridone and dipyridone appear to be further oxidized to yield a product tentatively identified as 4-carboxy-1-methyl-2-pyridone. With strong oxidizing conditions hydrogen peroxides oxidized paraquat to oxalic acid. No information was found to describe toxicity of any products except oxalic acid (sodium oxalate has a subcutaneous LD_{Lo} of 100 mg/kg for mice) (4). Also, reaction conditions are not available.



Faust and Gomaa have examined paraquat oxidation with permanganate, chlorine dioxide, and hypochlorite (102). While they did not perform a complete product study, they speculated that final products consisted of ammonia and either carbon dioxide (oxidation in acidic media) or oxylate (oxidation in alkaline media). These assigned products are non-toxic (4). Their assumption regarding products is probably valid for very strong oxidizing conditions.

The oxidation with permanganate yields MnO_2; the Registry (4) lists its toxicity as LD_{Lo} = 45 mg/kg (intervenous) for rabbits.

Oxidation was fastest in alkaline media. ClO_2 oxidation was too fast to measure in the pH range 8.14 to 10.15. With aqueous chlorine (HOCl) and permanganate the oxidation was rapid, but could be measured. The observed second order rate constants (at 20° and in pH buffers) were for permanganate 6.56 $\ell/\text{mole}^{-1}\text{min}^{-1}$ at pH 9.13 and for aqueous chlorine $5.75\text{x}10^{-3}$, $1.70\text{x}10^{-2}$ and $3.02\text{x}10^{-2}$ $\ell/\text{mole}^{-1}\text{min}^{-1}$ at pH8.14, 9.04, and 10.13, respectively. The complete oxidation requires very large volumes of oxidant for completion: stoichiometers are

$$(C_{12}H_4N_2)^{2+} + 14\ MnO_4^- \longrightarrow 14\ MnO_2 + 6\ C_2O_4^{2-} + 2\ NH_3 + 4\ H_2O$$

$$(C_{12}H_4N_2)^{2+} + 23\ ClO^- \longrightarrow 23\ Cl^- + 6\ C_2O_4^{2-} + 2\ NH_3 + 9\ H_2O$$

Although Faust and Gomaa did not determine stoichiometry for chlorine dioxide (ClO_2), it can be estimated from the expected Cl(IV) valence that complete oxidation will require less than 12:1 ratio of ClO_2 to paraquat. However, ClO_2 is too hazardous for use except by skilled technicians (101a). Complete oxidation with the other reagents will require massive volumes of decontaminant. If chlorine bleach (5% as HOCl) is used, it is estimated that paraquat (1.29 moles/ℓ) will require a minimum of 42 volumes of bleach (ca 0.7 moles/ℓ as HOCl). If 80:1 (vol/vol) of bleach is used, the calculated 99.9% degradation time, $t_{0.999}$, is calculated as 438 days at pH 10.13. For 0.5 molar $KMnO_4$ (the approximate solubility limit) the oxidation will require a minimum of 36:1 ratio of oxidant to paraquat. For 70:1 (vol/vol) of 0.5 molar $KMnO_4$: paraquat, $t_{0.999}$ is about 6.5 hours.

In conclusion, no chemical method is recommended for paraquat detoxification. Insufficient information is available to evaluate the product toxicity from its chemical hydrolysis. Chemical oxidation requires very excessive volumes of detoxicant. Reaction time with aqueous chlorine is too slow. The non-chemical disposal procedures recommended by EPA are recommended for paraquat disposal (7a). Its containers should be rinsed by the NACA recommended procedure (Section 3).

B.16 CHEMICAL METHODS FOR DETOXIFICATION OF PENTACHLORONITROBENZENE (PCNB)

PCNB (Terrachlor) is applied as a soil fungicide and seed treatment. It has a very low solubility in water (0.44 ppm at 20°C), is slightly soluble in alcohol (2% at 25°C), and is soluble in ketones and aromatic and chlorinated hydrocarbons. It is formulated as a 24% emulsifiable concentrate (2 lb/gal), dust (6.25, 10, 20, 40, and 75% wettable powder). PCNB is very stable in soil (15, 103, 104).

Strong alkali hydrolyzes PCNB to pentachlorophenol (PCP) and nitrite (28):

$$C_6Cl_5NO_2 + OH^- \longrightarrow C_6H_5OH + NO_2^-$$

PCP, which is also a pesticide, was reviewed by Shih and Dal Porto (1). PCP is more toxic than PCNB; comparative oral toxicities (LD_{50}) for rats are 1650 and 27 mg/kg (4). Since PCP should be disposed by land burial, the hydrolysis is not a useful detoxification method.

PCNB is reduced to the amine by stannous chloride and sulfuric acid (104):

$$C_6Cl_5NO_2 \xrightarrow[H_2SO_4]{Sn(II)} C_6Cl_5NH_2$$

No data was found on the toxicity of pentachloroaniline. Since many anilines are carcinogenic (67), it is concluded that pentachloroaniline is possibly carcinogenic.

PCNB and empty containers should be disposed by an EPA recommended procedure (7a). Bottles and drums should be triple rinsed with water and the rinse water used for a diluent if possible.

B.17 CHEMICAL METHODS FOR DETOXIFICATION OF DNBP (DINITRO-s-BUTYLPHENOL)

DNBP (Dinoseb) is applied as a pre- and post-emergence herbicide for weeds and grasses, as a desiccant for field crops, as a topical weed control, and for blossom thinning in fruit trees. DBNP is a nitrophenol. While the free acid is relatively water insoluble (0.005 g/100g), it forms water soluble salts. Dinoseb is soluble in ethanol (48 g/100g) and miscible with toluene and ether. It is corrosive to common metals (15, 18).

DNBP is formulated as the free acid in a 5 lb/gal emulsifiable concentrate and as alkanolamine salt (3 lb/gal as dinoseb). Several dinoseb esters are also marketed which include carbonic acid diesters, the acetate ester, and the methacrylate ester. Also, dinoseb analogs contain other alkyl groups substituted for the *sec*-butyl at the *ortho* position; these include dinocap (*sec*-octyl) and dinex (cyclohexyl) (14, 28). DNBP reacts with alkylating agents, oxidizing agents and reducing agents. Diazomethane reacts with it to yield the methyl ether (105). Acyl chlorides convert dinoseb to esters (28). The *s*-butyl group is oxidized to the benzoic acid with permanganate or chromate, but the product's toxicity is not known. Very strong oxidants can oxidize the nitro groups to produce quinones. Reducing agents convert nitro groups to amines (106). None of these reactions are practical disposal operations, in part, because they require some advanced technical skills.

Although environmental degradation is not well known, DNBP appears resistant to biodegradation (106). The free acid is the preferred state if DNBP is land disposed, since salts such as the alkanolamine are expected to be transported more rapidly with moving ground water.

DNBP and its empty containers should be disposed by an EPA recommended procedure (7a). Empty bottles and drums should be triple rinsed by the NACA recommended method (Section 3).

B.18 CHEMICAL METHODS FOR DETOXIFICATION OF CHLOROPICRIN

Chloropicrin is a stored grain and soil fumigant. As a soil fumigant it is applied for pre-planting control of insects, nematodes, fungi, and weed seeds. Chloropicrin is soluble in water at 2.27 g/ℓ at 0°C, and is miscible with acetone, methanol, carbon tetrachloride, and benzene. Chloropicrin boils at 112°C (233.6°F). The liquid is available in glass bottles (15, 107). It is also formulated with methyl bromide and chlorinated C_3 hydrocarbons (16).

Brozone: CH_3Br 68.6%; CCl_3NO_2 1.4%
Dowfume MC-2: CH_3Br 98%; CCl_3NO_2 2%
Dowfume MC-33: CH_3Br 67%; CCl_3NO_2 33%
Telone C: CCl_3NO_2 15%

Chloropicrin is relatively stable toward hydrolysis in water, dilute acid and dilute base. But, it does react with some very strong acid and base systems. Fuming sulfuric acid at 100°C reacts with chloropicrin to yield phosgene and nitrosyl chloride (108), which are more toxic than chloropicrin (4). Sodium or potassium methylate hydrolyze chloropicrin to non-toxic products (107):

$$CCl_3NO_2 + 4C_2H_5ONa \longrightarrow 3NaCl + NaNO_2 + C(OC_2H_5)_4$$

But, preparing methylate (adding metallic sodium or potassium to ethanol) and reacting methylate with chloropicrin are dangerous reactions (38).

Iodide, either as hydriodic acid or alkali iodide, degrades chloropicrin (108). The hydriodic acid reaction yields ammonia, carbon dioxide, chloride ion and iodine. Iodide salts will yield carbon tetraiodide. Neither reaction is judged suitable. Hydriodic acid is a hazardous reagent (38). Carbon tetraiodide, like carbon tetrachloride, might be carcinogenic (4).

Hot alcoholic sodium peroxide oxidizes chloropicrin. Products are sodium carbonate, nitrate, and chloride ion (109).

When chloropicrin is heated at 100°C with ammonia for several hours, it yields guanidine (108). Since guanidine is non-toxic, the method has been recommended for detoxification (3). However, several of the alternatives are judged more practical. A good alternative consists of heating chloropicrin with potassium acetate and alcohol at 100°C; products are potassium carbonate, ethyl acetate, and chloride ion (108). All products are non-toxic (4).

Chloropicrin reacts quite smoothly with sulfides and trisubstituted phosphines at ambient temperatures (28, 108). Although reaction with free mercaptans is slow, reaction is rapid with alkali mercaptides. Products with mercaptides are the corresponding disulfide and a mixture of carbon dioxide and nitrogen (major) and carbon monoxide and nitrous oxide (minor). Although the minor products (CO and NO) are slightly toxic, they are less toxic than chloropicrin (4). The reaction between chloropicrin and trisubstituted phosphines yield parallel products: the corresponding phosphonic dichlorides and a mixture of carbon dioxide and nitrogen or carbon monoxide and nitrous oxide. The method is not judged practical since the reagents (mercaptans or trisubstituted phosphines) are noxious and require some skills for handling (38).

Chloropicrin is reduced by iron filings to yield methylamine and chloride ion (110). The reaction requires an aqueous acid media to reach completion. Some technical skill is required to maintain proper temperature, since the reaction is quite exothermic. The recommended procedure is to slowly add the chloropicrin to a cooled mixture of fine iron filings in aqueous acid.

Chloropicrin is photoreactive (108). An interesting reaction occurs when chloropicrin solution (methanol, ethanol, acetic acid, benzene) is left in sunlight. After one day of exposure the chloropicrin is reduced to ammonia and unknown organics. The reaction does not take place in the dark.

Chloropicrin is not inflammable (111). While it could be incinerated, this would require the addition of fuel. Recommended conditions are a primary combustion at 1,500°F for 0.5 seconds minimum and secondary combustion at 2,200°F for 1.0 second minimum. The incineration products are very corrosive and must be scrubbed (111).

Chloropicrin should be disposed by an alternative, EPA recommended procedure (7a). Bottles should be thoroughly drained and triple rinsed by the NACA recommended procedure (Section 3).

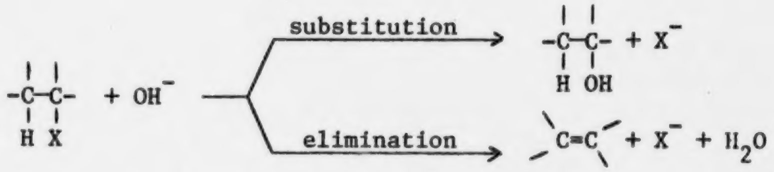
APPENDIX C.

CHEMICAL METHODS FOR THE DETOXIFICATION OF HALOGEN-CONTAINING PESTICIDES

C.1 GENERAL REVIEW OF APPLICABLE DISPOSAL METHODS

The halogenated hydrocarbon pesticides encompass a wide range of chemical structures (Table 30). Their hazards are often, but not always, associated with the halogen content. Since dehalogenation is the usual detoxification approach (1, 2), a general review of this subject is presented in this section. Pesticides which can be detoxified by other approaches will be discussed on a case-by-case basis.

Dehalogenation can be achieved by a variety of ionic and reductive processes. The ionic reactions discussed herein are characterized as nucleophilic (48). The most useful nucleophilic reagent is hydroxide, which reacts fairly readily with aliphatic halogen to yield substitution and elimination products.



Stronger electrophiles such as the alkoxides (methoxide, ethoxide) and amide react with aliphatic halides in the same way to produce analogous products. They also react with olefin and aromatic halogen:

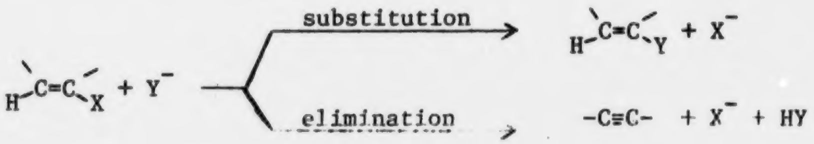


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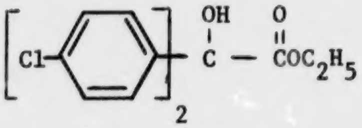
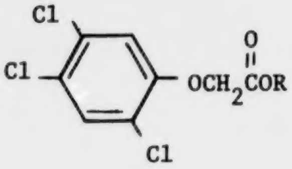
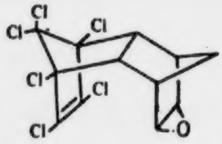
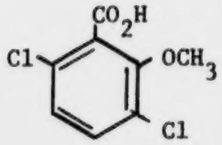
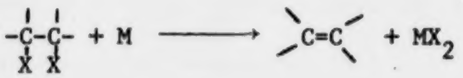
Table 30. Chemical Structures of Selected Halogen-Containing Pesticides.

NAME	STRUCTURE	MW
DDT Relatives Chlorobenzilate	 Cl 2 OH C O COC2H5	325.2
Chlorophenoxy derivatives 2,4,5-T	 Cl Cl Cl O OCH2COR	255.5 (R=H)
Aldrin-Toxaphene group Endrin	 Cl Cl Cl Cl Cl Cl O	380.9
Aliphatic brominated hydrocarbons Dibromochloropropane (DBCP)	$BrCH_2CHBrCH_2Cl$	236
Aliphatic and Alicyclic Chlorinated Hydrocarbons		
Benzene hexachloride (BHC)	$C_6H_6Cl_6$	290.8
D-D	Mixed dichloropropanes & dichloropropenes	
Highly Chlorinated Aromatics Dicamba	 CO2H Cl OCH3 Cl	221.0

Potentially useful nucleophilic reagents for pesticide detoxification include alkali amides, sodium biphenyl, and alkali alkoxides (methoxide, ethoxide, etc.) (3, 113, 114). Strong acids participate in electrophilic reactions by assisting in ionization of halide and by catalyzing rearrangement reactions (48).

Catalytic hydrogenation will dehalogenate practically any chlorinated hydrocarbon; however, dehalogenation requires highly sophisticated equipment, expensive catalytic reagents, and well trained technicians. Catalytic hydrogenation requires heating the pesticide within a hydrogen atmosphere in the presence of a transition metal catalyst (3, 48). Since it is not practical, proposals to use it for the selected pesticides will not be discussed further.

Halogenated hydrocarbons can be degraded by a variety of reducing agents. Alkyl halides are reduced by hydride transfer agents, such as lithium aluminum hydride and with reactive metals and metal complexes, such as magnesium or chromous chloride (48). Vicinal dihalides will reductively dehalogenate to yield olefins with metals (sodium, zinc, etc.), metal hydrides (e.g., $LiAlH_4$), and other reducing agents (e.g., iodide) (48, 115).

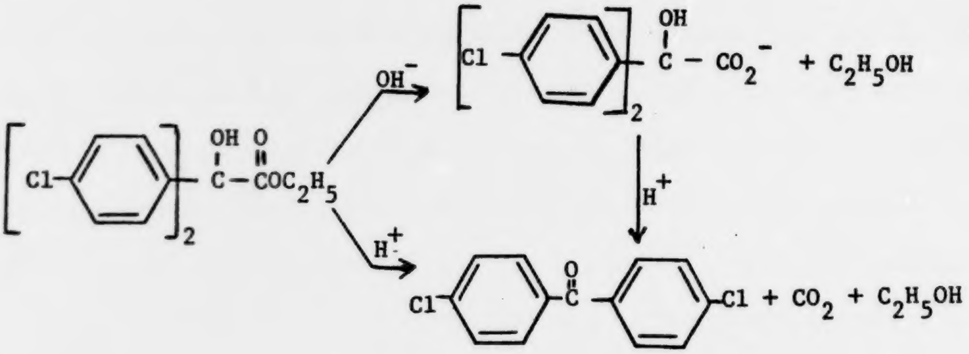


Although dechlorination could be achieved with almost all the halogenated pesticides, it is not practical as a general approach. Most of the reagents are expensive and too hazardous for general use. Stronger caustics than 10 to 20% sodium hydroxide are considered too hazardous for general use. Many of the reagents used for reductive dechlorinations are pyroforic, for example, sodium metal (38).

C.2 CHEMICAL METHODS FOR DETOXIFICATION OF CHLOROBENZILATE

Chlorobenzilate is an acaracide used for a variety of agricultural crops and on ornamentals. The most common formulations are emulsifiable concentrates. Other formulations include a 25% wettable powder, and 3% dust. Chlorobenzilate is practically insoluble in water, but soluble in alcohol, acetone, and xylene (15, 23).

Chlorobenzilate can be hydrolyzed by strong acid or alkali (2). The initial product from alkaline hydrolysis is sodium chlorobenzilate. If this sodium salt is neutralized or if chlorobenzilate is hydrolyzed in acid media, the intermediate chlorobenzilic acid rapidly decarboxylates to yield p,p'-dichlorobenzophenone.



Chlorobenzilate has a relatively low acute hazard (oral LD_{50} = 700 mg/kg for rats), but, it has yielded a positive test as a carcinogen (4). The only toxicity information found for p,p'-dichlorobenzophenone is its reported interperonital LD_{50} of 200 mg/kg (for rats). It is not clearly certain that this method does represent a significant detoxification of chlorobenzilate. Its advantage is that no evidence would suggest that dichlorobenzophenone is carcinogenic. But, it does not seem to substantially reduce acute hazard.

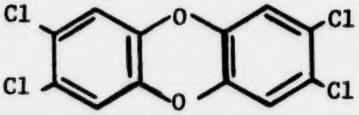
No evidence was found concerning the environmental fate of dichlorobenzophenone. Based on the evidence at hand, the chronic exposure hazard from chlorobenzilate is judged minimal, so, hydrolysis is not recommended.

Chlorobenzilate can be dechlorinated by sodium in isopropyl alcohol. The organic products have not been identified (23).

Chlorobenzilate should be disposed by the EPA recommended procedures as an alternative to chemical detoxification (7a). Empty bottles and drums should be thoroughly drained and rinsed by the NACA recommended method (Section 3).

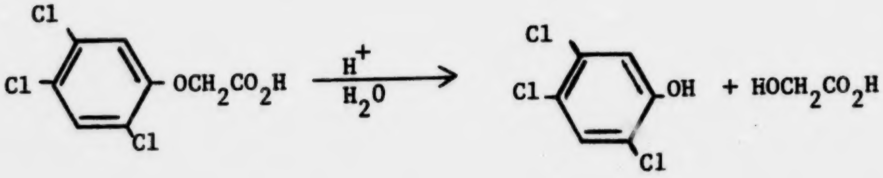
C.3 CHEMICAL METHODS FOR DETOXIFICATION OF 2,4,5-T

2,4,5-T (2,4,5-trichlorophenoxyacetic acid) is a selective herbicide, which is used primarily for brush and broadleaf weed control (15, 45). The free acid has only a slight water solubility (278 ppm) and is soluble in acetone and ethanol. Most 2,4,5-T is formulated as derivatives of the free acid. Aqueous formulations contain the water soluble salts of amines or alkanolamines and formulations in petroleum oil are prepared from esters (15). 2,4,5-T contains trace quantities of a highly toxic teratogen, 2,3,7,8-tetrachloro-*p*-dioxin (TCDD). The technical material is contaminated by less than 0.5 ppm of TCDD, while its threshold toxicity appears about 30 ppm (91).



2,3,7,8-tetrachloro-*p*-dioxin (TCDD)

The chemical and physical properties of 2,4,5-T are analogous to 2,4-D (1, 91). 2,4,5-T is cleaved by strong acid to 2,4,5-trichlorophenol, formaldehyde, and carbon dioxide; glycollic acid appears to be an intermediate (91).



$$HOCH_2CO_2H \longrightarrow CH_2O + CO + H_2O$$

This hydrolysis requires heating with concentrated acid or pyridine hydrochloride. 2,4,5-T is completely degraded by alkali metals (Na or Li) in liquid ammonia, but the degradation products have not been identified. Chlorination is capable of destroying 2,4,5-T. Aqueous hypochlorite at pH 3 and temperatures above 85°F will yield herbicidally inactive products, but the products have not been characterized (113, 114). At high temperature (about 400°C) chlorinolysis can degrade 2,4,5-T to a mixture of carbon tetrachloride, phosgene, and hydrogen chloride (116). None of these reactions are practical detoxification approaches for 2,4,5-T.

Chemical treatment is not considered a viable approach for degrading the trace quantities of TCDD. Cleavage of the ether and dechlorination requires highly reactive chemical reagents, such as strong acid or sodium amide (48).

Both 2,4,5-T and TCDD are degraded by photochemical reactions (91, 117). TCDD will degrade to non-toxic products in sunlight provided an organic hydrogen donor is available. This photochemical reactivity has been proposed for TCDD and other chlorinated dioxin spills (118). The degradation will be completed in a matter of days, if sufficient sunlight is available.

2,4,5-T is detoxified by microbial activity in a period of 45 to 270 days (91). The biodegradation is most rapid in warm, aerated, moist soils, and aerobic activity is preferred. TCDD is relatively persistent in soil. Kearney and coworkers report that approximately 60% was recovered after 1-100 ppm TCDD was incubated for one year in loamy sand or silty clay loam (117). It would appear that TCDD could build up in soil if 2,4,5-T containing trace amounts of TCDD were disposed by land burial.

In summary, no practical chemical detoxification procedures are now available for waste 2,4,5-T. The photochemical degradation to remove traces of TCDD is an interesting approach for spill clean-up but not for disposal. The photochemical method could conceivably result in vaporization of the volatile 2,4,5-T esters. So, it was only suggested as a possible detoxification approach for accidental spillage.

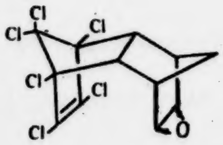
Shih and Dal Porto have recommended that free acid and salts of 2,4-D should be precipitated from liquid formulations with calcium or magnesium salts to reduce transport with groundwater (1). This method would also mitigate migration if 2,4,5-T were disposed by land burial.

The EPA recommended procedures should be used as an alternative to chemical detoxification for disposal of 2,4,5-T and its containers (Section 3) (7a).

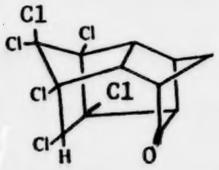
C.4 CHEMICAL METHODS FOR DETOXIFICATION OF ENDRIN

Endrin is an insecticide for cotton pests and other field crops. It has also been applied for mouse control. Endrin is almost insoluble in water and is sparingly soluble in alcohols. It is formulated in wettable powders (25% and 50%), dusts and granules and a 1.6 lb/gal emulsifiable concentrate (15, 23).

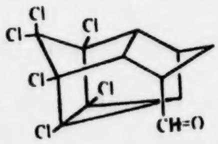
Endrin is a chlorinated dicyclopentadienyl pesticide which has analogous chemical reactivity to other members of this class, such as aldrin and dieldrin. It is not reactive with alkali or weak acids. Endrin has a double bond which undergoes typical olefinic reactions, such as halogenation and oxidation. But, reaction products have not been well characterized. Endrin (I) undergoes skeletal rearrangements and dechlorinations as the result of thermal treatment, ultraviolet irradiation, reactions with Lewis and Bronsted acids (including boron trifluoride and sulfuric acid) and chemical reduction (119, 120). Mixtures of less toxic products are formed by thermal treatment (200°C or higher), mild heating (less than 100°C) with acids (including BF_3, $ZnCl_2$ plus HCl, H_2SO_4, and $HClO_4$) or ultraviolet irradiation (119, 121-123). The products are ketone II, aldehyde III, and alcohol IV. Oral toxicities (rats) are reported at 62.1 and 500 mg/kg for II and III, respectively (120, 121). No toxicity information was found for IV. In comparison, oral LD_{50} for endrin is 3 mg/kg.



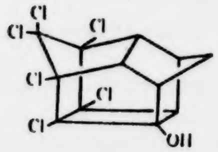
I



II

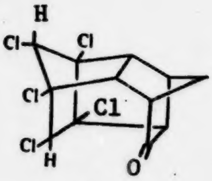


III



IV

Endrin is reductively dechlorinated. Sodium methoxide in dimethyl sulfoxide dechlorinates the anti-position of the bridge dichloromethano-group without skeletal rearrangement (119). Metallic reducing agents initially convert endrin to Δ-keto endrin, structure II, before reducing the anti-chloride to yield ketone V. Reducing agents yielding V include zinc plus acid or chromous chloride (119). Sweeny and Fisher reduced endrin with zinc dust and zinc-copper couple in an acetic acid-acetone mixture for 21 to 22 hours (125). About 10% of the initial endrin remained and only 25% of the theoretical chlorine was identified as soluble chloride.



V

Ultraviolet irradiation also can reduce endrin. Its irradiation in hexane solution yielded a product with hydrogen replacing one of the bridgehead chlorides. Perumal has evaluated products from irradiation of the chlorinated dicyclopentadienyl derivatives and obtained products with reduction of anti-position of the dichloromethano-bridge analogous to structure V (126).

Although endrin is chemically converted to products of lower acute toxicity, none of the methods are suitable for recommendation at this time. The reagents and conditions required are judged too advanced for general recommendations. The addition of metals or their salts, such as zinc or iron, show promise, but more information is required. Also, chronic effects of the rearranged products should be examined.

The EPA recommended procedures should be used for disposal of endrin and its containers (7a). Empty bottles and drums should be triple-rinsed by the NACA recommended method (Section 3).

C.5 CHEMICAL METHODS FOR DETOXIFICATION OF DIBROMOCHLOROPROPANE

Dibromochloropropane (DBCP) is a soil fumigant used for nematode control. It is formulated as emulsifiable and non-emulsifiable concentrates, and granules. The most popular formulation contains 12.1 pounds active ingredient per gallon (14, 15). DBCP has a water solubility of 1 g/kg at ambient temperature and is miscible with alcohols and acetone. It boils at 196°C (15).

DBCP is stable in dilute acid and neutral solutions, but is hydrolyzed in alkaline solution. The products depend upon the hydrolysis conditions. It is easily hydrolyzed to 2-bromoallyl alcohol in aqueous base (104, 127).

$$BrCH_2CHBrCH_2Cl \xrightarrow{OH^-} CH_2 = CBrCH_2Cl \xrightarrow{OH^-} CH_2 = CBrCH_2OH$$

But, since the product, 2-bromoallyl alcohol, is a vinyl halide, it could be carcinogenic (67). With more vigorous conditions, the vinylic bromide is further degraded to acetylenic derivatives. Reflux with aqueous caustic will yield propargyl alcohol (125, 127).

$$H_2C{=}CBrCH_2OH \xrightarrow{OH^-} CH{\equiv}CCH_2OH + H_2O + Br^-$$

The toxicity of propargyl alcohol is very high; oral LD_{50} for rats is listed as 70 µg/kg (4). DBCP hydrolysis in potassium ethoxide (prepared by adding potassium metal to ethanol) yields ethyl propargyl ether (127).

$$BrCH_2CHBrCH_2Cl \xrightarrow[C_2H_5OH]{KOC_2H_5} HC{\equiv}CCH_2OC_2H_5$$

Although no toxicological data was found for this ether, the relatively low toxicity (oral LD_{50} of 539 mg/kg for rats) of dipropargyl ether, $(CH{\equiv}CCH_2)_2O$, suggests that ethyl propargyl ether will have a low toxicity. Kennedy and coworkers achieved 100% DBCP degradation with sodium or lithium metal in liquid ammonia-hexane (114). The products were not characterized. Rauscher reports that aliphatic halides are extensively dehalogenated by sodium ethanolamine in dioxane, but organic products were not identified (128). Rauscher prepared the reagent by adding metallic sodium to a monoethanolamine-dioxane mixture.

DBCP can be dehalogenated by metallic reducing agents. Kray and Castro have reduced DBCP to propylene with chromous chloride in 2:1 water-dimethylformamide (DMF) (129, 130). The conversion proceeds in two steps. DBCP rapidly reductively debrominates to yield allyl chloride which is subsequently

$$2Cr^{2+} + CH_2BrCHBrCH_2Cl \longrightarrow CH_2{=}CHCH_2Cl + 2CrBr^{2+}$$

$$Cr^{2+} + CH_2{=}CHCH_2Cl \longrightarrow CH_2{=}CHCH_3 + CrCl^{2+}$$

reduced to propene. They measured kinetics for the allyl chloride reduction at 29.7°C. The rate was second order:

$$\text{Rate} = k_2 [Cr^{2+}][C_3H_5Cl]$$

with $k_2 = 1.2 \pm 0.1$ ℓ/mole-min.

Zinc-acid mixtures could be an effective reagent for DBCP dehalogenation. Zinc with either acetic or hydrochloric acid is a commonly used reducing agent for dehalogenation (48, 131). This reagent is well known for debrominating vicinal bromides and is capable also of removing halide from vinylic carbon. Although zinc-acid reagents have been used for extensive dehalogenation of pesticides, no information on its use for DBCP was found (125, 132).

None of the current methods are acceptable for DBCP detoxification. All require hazardous reagents and fairly sophisticated techniques. The EPA recommended procedures should be used for disposal of DBCP and its containers (7a). Containers should be triple-rinsed by the NACA recommended procedure (Section 3). The manufacture recommends that DBCP should be incinerated, if possible (133). Its incineration requires dilution with inflammable solvent and facilities to scrub the HCl and HBr evolved.

C.6 CHEMICAL METHODS FOR DETOXIFICATION OF BHC

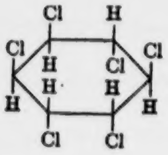
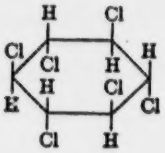
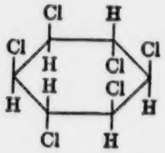
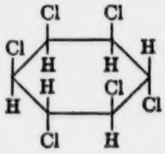
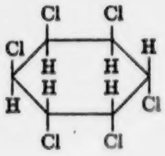
BHC is also known by several alternative names: benzene hexachloride, HCH, and hexachlorocyclohexane. BHC is a mixture of stereoisomers of 1,2,3,4,5,6-hexachlorocyclohexane and a trace amount of related chlorinated cyclohexanes. The most important constituent is the γ-BHC isomer, lindane. Currently, BHC is being phased out as a pesticide, but purified lindane is remaining. Lindane is the dominant isomer which influences BHC insecticidal activity. BHC (and lindane) are formulated in numerous products, both as the sole active ingredient and combined with other active ingredients. The formulations include emulsifiable concentrates, dusts, granules, and oil solubles. Percentages generally range from 0.1 to 20%. Applications include seed treatment, animal pest control, and forestry (14, 141).

Table 31 describes the major constituents of BHC. BHC is also formulated with increased lindane content. A complete description of chemical behavior and physical properties would require evaluation of each isomer. Since this is beyond the scope of this report, a general review of gross behavior of the mixture and only salient properties of the individual isomers is presented herein. The mixture behaves as expected for chlorinated hydrocarbons. Reactivity differences arise primarily from stereochemical constraints within the cyclohexane structure. For a detailed discussion one of several reviews should be consulted (119, 135).

Isomers range in solubility: 0.5×10^{-4} to 1×10^{-4} g/100g in water; 1.1 to 24.2 g/100g in ethanol; 1.1 to 41.1 g in benzene; and 7.9 to 71.1 g/100g in acetone (28).

BHC is relatively stable to chemical oxidation. It does not react with chlorine, peroxide (H_2O_2 or Na_2O_2), and permanganate, but is degraded by ozone

Table 31. Description of BHC Composition. Adapted from Melnikov (28) and Gunther and Blinn (152).

ISOMER	STRUCTURE	PERCENTAGE
α		65-70
β		6-8
γ		12-15
δ		2-5
ε and other chlorinated cyclohexanes		3-7

to unspecified products (150, 151). It can be catalytically dehydrogenated to yield hexachlorobenzene (28, 135).

Reducing agents dechlorinate BHC and yield benzene. The zinc-acetic acid system is a well known reagent for this reduction (132, 135). The zinc-acetic acid reduction is not recommended as a general detoxification method. The product, benzene, has a relatively low toxicity (oral LD_{50} of 756 mg/kg for rats), but it is a suspected carcinogen (4). Also, the alkyl halide dechlorination reaction with zinc and acetic acid generates heat and frothing when it is performed as bulk reaction (137).

BHC is stable toward hydrolysis in neutral and acid media. BHC does hydrolyze very slowly at room temperature; only 0.13% of the HCl is lost by the γ-isomer after heating at 102° for 1 hour (28). Although BHC is generally inert to aqueous acids, some reactions occur with very powerful acids. Chlorosulfonic acid can degrade it to benzene and other products (119). Also, Lewis acids, such as aluminum chloride, catalyze the isomerization between the BHC isomers to yield new compositions (28).

Alkaline media (and nucleophilic reagents such as amines) will hydrolyze all BHC isomers except the β-isomer (138, 139). The stability of the β-isomer results from stereochemical relationship of the chloride atoms. The products are trichlorobenzene isomers. Yields ranged from 60 to 80%, 4 to 10%, and 6 to 15% for 1,2,4-, 1,3,5- and 1,2,3-trichlorobenzene, respectively (119).

The hydrolysis rates (with the exception of the β-isomer) are amenable to practical detoxification. Cristol has delineated the kinetics (139). Hydrolysis is second order: first order both in BHC and hydroxide. Table 32 summarizes apparent first order rate constants for the hydroxide reaction in aqueous ethanol.

$$C_6H_6Cl_6 + 3OH^- \xrightarrow{k_{obs}} C_6H_3Cl_3 + 3H_2O + 3Cl^-$$

Table 32. Apparent First-Order Rate Constants For Hydrolysis Of BHC Isomers To Trichlorobenzene With Sodium Hydroxide In 76.1% Ethanol At 20.11%.

Isomer	k_{obs} (ℓ/mole-sec.)
α	0.167 - 0.172
β	$3x10^{-6}$
γ	0.0435 - 0.0457
δ	0.106 - 0.113

Time for 99.9%, $t_{0.999}$, BHC degradation (with the exception of the β-isomer) can be calculated from Equation A-7 with n = 3. Approximate $t_{0.999}$ was calculated for BHC hydrolyzed with 1N hydroxide in 50% aqueous ethanol. $t_{0.999}$ was calculated for 1 pound of BHC mixed with 3.7 ℓ (1 gal) of detoxicant and an estimated rate constant of 0.044 ℓ/mole-sec (k_{obs} for the γ-isomer). These parameters yield $t_{0.999}$ of approximately 3.5 minutes. The trichlorobenzenes have an advantage with respect to known toxicities. The acute oral LD_{50} of 1,2,4-trichlorobenzene is 756 mg/kg for rats. In comparison, γ-BHC has an oral LD_{50} of 88 mg/kg for rats. Also, BHC has yielded positive tests for carcinogenesis, while the chlorobenzenes are not known to produce any long-term exposure effects (4, 67). Disadvantages of alkaline hydrolysis include its inability to degrade the β-isomer.

Except for the β-isomer, BHC appears to metabolize in the environment (140, 141). β-BHC which is persistent accounts for about 7% of technical BHC. BHC metabolites which have been identified include chlorinated phenols, chlorinated benzenes and has chlorinated cyclohexanes. The trichlorobenzenes are environmentally persistent and capable of bioaccumulating (142-145).

In conclusion, alkaline hydrolysis does offer a moderate reduction in acute toxicity. Although the hydrolysis products are not at this time, suspected carcinogens, they apparently bioaccumulate. Because the hydrolysis products are a potential hazard, the method is not recommended. Instead, an alternative, non-chemical method in accordance with the EPA recommendations should be used for disposal (7a). Empty bottles and drums should be tripe-rinsed by the NACA recommended method (Section 3).

C.7 CHEMICAL METHODS FOR DETOXIFICATION OF D-D

D-D is a soil fumigant which consists of a mixture of chlorinated C_3 hydrocarbons; it is primarily used as a pre-plant nematocide. D-D composition is (28):

cis-1,3-dichloropropene	30-33%
trans-1,3-dichloropropene	30-33%
1,2-dichloropropane	30-35%
Trichloropropanes plus more highly chlorinated products	up to 5%

D-D distills in the range 95-150°C. It is soluble in water at 2 g/ℓ (104).

Chemical reactivity corresponds to expected behavior for chlorinated aliphatic hydrocarbons, but information is not well developed. The manufacturer reports that it reacts with dilute inorganic bases, concentrated acid, metal salts, and active metals, but does not describe the products (2, 146). Product information can be derived from known chemistry of the major components.

The major components are the cis and trans isomers of 1,3-dichloropropene. These allylic chlorides are easily hydrolyzed with hydroxide to yield 1-chloropropen-3-ol (127). α-Chloroallylic alcohol will eliminate HCl when treated with base in vigorous conditions. The product is propargyl alcohol, $CH{\equiv}CCH_2OH$, which has a high oral toxicity (See Section C.4). The dichloropropenes will react with potassium ethoxide or potassium acetate, to yield the corresponding ether ($C_2H_5OCH_2CH{=}CHCl$) and ester ($CH_3CO_2CH_2CH{=}CHCl$), respectively. Dichloropropene is not reactive with fuming sulfuric acid at 100° to 150° (127).

1,3-dichloropropane is not as reactive as the dichloropropenes (48, 127). It is relatively stable with sodium amalgam or zinc plus acetic acid. It reacts with potassium ethoxide to yield 1-chloropropene. It will hydrolyze with water at 210° to 220°C or at 150°C if heated with PbO and water. The initial product, propanediol will rearrange to yield acetone and propionaldehyde.

Since no suitable method of chemical detoxification is available the EPA recommended procedures should be followed for disposal of D-D and its containers (7a) (Section 3).

C.8 CHEMICAL METHODS FOR DETOXIFICATION OF DICAMBA

Dicamba (Banvel) is a post-emergence herbicide. It is used as the free acid or its salts, usually the dimethylamine salt. The free acid has water solubility of 4.5 g/ℓ at 25°C, is soluble in ethanol and acetone, and moderately soluble in xylene. The dimethylamine salt has a water solubility of 720 g/ℓ. Dicamba is marketed in several formulations including 4 lb/gal water soluble, 4 lb/gal oil soluble, and 5 and 10% granules. Also, it is combined with other herbicides in numerous formulations (14, 15).

Dicamba is chemically relatively inert (2). It is stable to oxidation and hydrolysis. The carboxylic acid can be derivatized, but the procedures would only be useful for analytical purposes (148). Kennedy and coworkers found that sodium or lithium with liquid ammonia in hexane will dehalogenate dicamba; products were not reported (113). Dicamba appears photochemically stable (149).

The EPA recommended procedures should be used for disposal of dicamba and its containers (7a) (Section 3). The manufacturer recommends disposal by land burial or incineration (150). If dicamba is land disposed, its conversion to the acid form could reduce its mobility in soil.

APPENDIX D
CHEMICAL METHODS FOR THE DETOXIFICATION OF INORGANIC AND METALLO-ORGANIC PESTICIDES

D.1 GENERAL REVIEW OF APPLICABLE DISPOSAL METHODS

The two pesticides selected, arsenic acid and MSMA (monosodium methanearsonate), characterize the inorganic and organometallic arsenicals, respectively. Disposal problems of the arsenicals reflect problems experienced with other metal and metalloid pesticides (2). The element, arsenic, is ubiquitous in the environment and exists in a wide variety of inorganic and organic compounds (151). Its environmental behavior parallels that of mercury (152).

Although arsenic will remain a toxic metal, its hazard can be mitigated. Highly toxic arsenic compounds can be degraded to compounds of lower toxicity. Leaching problems can be reduced by preparing precipitates which are either fixed or slowly release the arsenic. The reactions most important for disposal are oxidation-reduction and ion exchange.

D.2 CHEMICAL METHODS FOR DETOXIFICATION OF ARSENIC ACID

Arsenic acid which is applied as a cotton desicant and herbicide is marketed as a 75% (by weight) liquid concentrate (14, 153). Its solubility is 16.7 g/100 ml in cold water and 50 g/100 ml in hot water (154).

Arsenic acid is weakly amphoteric. Heavy metals will react with it to yield insoluble precipitates, some of which are used for quantitative analysis of As(V) oxides. Metals which quantitatively precipitate arsenic acid include magnesium, lead, calcium, and iron (III) (155, 156). Arsenate precipitation with ferric hydroxide has been suggested to reduce its phytoxicity (151). Its precipitation will also reduce its potential for leaching. Arsenate could be suitably precipitated with a slight excess of lime, ferric hydroxide, or magnesia. The best procedure is to stir ferric chloride, or a hydroxide of ferric, calcium, or magnesium into the waste arsenic acid and allow the mixture to stand 24 hours. Then, the supernatant water should be siphoned or decanted (2).

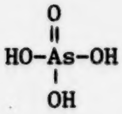
An alternative procedure would be to precipitate arsenic with sulfide. Since the method requires more sophisticated handling, the precipitation with heavy metals is preferred. The sulfide precipitation requires decreasing the solution acidity to less than pH 1 with 6N HCl, then saturating the solution with sodium sulfide or hydrogen sulfide (155). The precipitate and supernatant should be handled just as described for the ferric or other metal arsenate precipitates.

The EPA recommended procedures should be used for disposal of arsenic acid and its containers (7a). Empty containers should be triple-rinsed by the NACA recommended procedures (Section 3). Although the precipitation of arsenic acid could reduce its mobility in the environment and its toxicity, insufficient environmental testing is available to verify this conclusion. The precipitates should be considered hazardous. Any use of precipitation should only be in strict accordance with the EPA recommended procedures (7a).

D.3 CHEMICAL METHODS FOR DETOXIFICATION OF MSMA (Monosodium Methanearsonate)

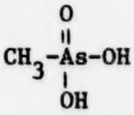
MSMA is a selective post-emergence contact herbicide. It is soluble in water (570 g/ℓ at 25°C) and in methanol. MSMA is formulated as 6 and 8 lbs/gal liquids (14, 15).

MSMA is a member of a group of methylated arsenic acid analogs. It is the monosodium salt of methanearsonic acid,



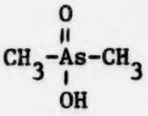
$\mathrm{HO{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{As}}{-}OH}$

Arsenic Acid



$\mathrm{CH_3{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{As}}{-}OH}$

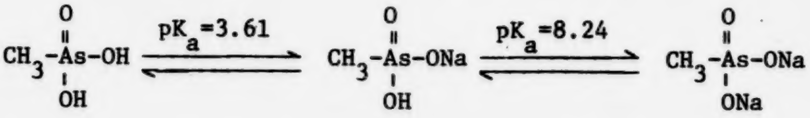
Methanearsonic Acid



$\mathrm{CH_3{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{As}}{-}CH_3}$

Cacodylic Acid

which is in equilibrium with the free acid and the disodium salt, DMSA (151).



$$\mathrm{CH_3{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{As}}{-}OH \xrightleftharpoons{pK_a=3.61} CH_3{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{As}}{-}ONa \xrightleftharpoons{pK_a=8.24} CH_3{-}\underset{\underset{ONa}{|}}{\overset{\overset{O}{\|}}{As}}{-}ONa}$$

Arsenic Acid MSMA DSMA

The methyl group of methanearsonic acid is stable to hydrolysis. It can be oxidized by heating it at 315°C in sulfuric acid or at lower temperatures in nitric acid-sulfuric acid mixtures (157-159). Methanearsonic acid can also be reduced to yield derivatives of trivalent arsenic. Its reaction with SO_2 in an aqueous halogen acid (HCl or HBr) yields the corresponding methylarsine dihalide (CH_3AsX_2). When it is reacted with a sodium sulfite-hypophosphorous acid mixture, it forms a polymeric sulfide, $[CH_3AsS]_n$. Methanearsonic acid reacts with H_2S to yield the pentavalent arsenic disulfide, CH_3AsS_2 (158, 159).

Methanearsonic acid quantititively precipitates with a wide variety of alkaline earth and transition metals. The metal salts exhibit amphoteric behavior; precipitation is pH dependent. For example, the quantitative precipitation occurs at pH 3 for Al(III), at pH 4 for Cu(II), pH 5 for Mn(II) or Fe(II), at pH 6 for Zn(II), at pH 7 for Fe(III), and at pH 8 for Mg(II) (158, 159).

The EPA recommended procedures should be used for disposal of MSMA and its containers (7a). Empty containers should be triple-rinsed by the NACA recommended procedures (Section 3). The precipitation of MSMA might reduce hazard if land burial is used for disposal. Since environmental fate of precipitated MSMA is not known, if used, it should be considered potentially hazardous and in accordance with the EPA recommended procedures (7a).

APPENDIX E
CHEMICAL METHODS FOR DETOXIFICATION OF MISCELLANEOUS PESTICIDES

E.1 GENERAL REVIEW OF APPLICABLE DISPOSAL METHODS

Miscellaneous pesticides selected for study are sodium fluoroacetate (Compound 1080), creosote, and warfarin. Their disposal will be discussed individually.

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E.2 CHEMICAL METHODS FOR DETOXIFICATION OF SODIUM FLUOROACETATE

Sodium fluoroacetate (Compound 1080) is applied as a rodenticide and for other mammalian predator control. Because fluoroacetate is extremely toxic, its use is restricted to government, research or laboratory, or licensed pest control operators (14). Sodium fluoroacetate is very water soluble and relatively insoluble in organic solvents, including acetone and alcohol (161).

Relatively little information was available describing the chemical reaction of fluoroacetate. The carboxylic acid group can be derivatized (to yield esters and amides), which are about as toxic (162). The alkyl-fluoride bond is chemically relatively stable (48). Methods for chemical hydrolysis of the other alkyl halides either do not affect alkyl fluorides or hydrolyzes them slowly. Aqueous fluoroacetate solution loses toxicity relatively slowly, which indicates some hydrolysis (162). Powerful bases, such as sodium amide, are capable of breaking the C-F bond in fluoroacetate. The C-F bond is also relatively inert to oxidation (48).

Land burial is a dangerous disposal method even though fluoroacetate will metabolize in the soil (161). David and Gardner evaluated the time required until residues showed no toxicity when fluoroacetate was incubated in loam soil. This required 2 and 11 weeks for 10 and 50 ppm fluoroacetate, respectively (164). Higher fluoroacetate could conceivably result in longer periods. Another hazard is that fluoroacetate can be translocated into plants or be transported with ground water. When fluoroacetate is metabolized, it yields fluoride ion. Fluoride is toxic, although far less toxic than fluoroacetate. For sodium fluoride, oral toxicities are reported as LD_{Lo} of 4 to 75 mg/kg for humans and

LD_{50} of 180 mg/kg for rats (4). Fluoroacetate and its containers must be disposed by a non-chemical alternative as described in the EPA recommended procedures (Section 3) (7a). The manufacturer will accept fluoroacetate for reprocessing (163).

E.3 CHEMICAL METHODS FOR THE DETOXIFICATION OF CREOSOTE

Creosote is a wood preservative derived from coal tar. The material is prepared to conform to a specific distillation standard (American Wood Preservers Specification P1-65) (14, 165, 166). Creosote contains more than 200 separate constituents, most of which are polynuclear aromatic hydrocarbons (PAH). Less than 20 constituents account for at least 75% of the creosote. Lorenz and Gjovik have identified the major constituents and their approximate percentage by gas chromatography; Table 33 summarizes their results (167).

Most of the constituents identified are PAH with three or more rings, less than 10% are naphthalenes and biphenyl. Two constituents (carbazole and dibenzofuran) have heteroatoms (oxygen and nitrogen, respectively). The mixture is high boiling (greater than 200°C) and has a very low water solubility (164).

PAH's are suspected carcinogenic agents (168, 169). One component, chrysene, is a known carcinogen, while others including the largest single component phenanthrene are suspected carcinogens. The PAH's are naturally produced and ubiquitous in the environment. Evidence has been presented that they can bioaccumulate. They can be biologically degraded, but the rate appears to be slow (168, 169). Since it is beyond the scope of this study to detail reactivity of all known constituents, general chemistry of the important constituents is reviewed.

Several groups have examined oxidation of PAH's by chlorine, chlorine dioxide, and ozone (168, 170-172). These studies have been concerned with the removal of PAH's from water in typical water treatment plants. The studies have demonstrated that PAH's are oxidized and removed from water. Benzpyrene yielded non-carcinogenic products with chlorinolysis; however, products were

Table 33. Major Components in Creosote.
Adapted from Lorenz and Gjovik (167)

Component	Approx. Pct. ±0.7%
Naphthalene	3.0
2-Methylnaphthalene	1.2
1-Methylnaphthalene	.9
Biphenyl	.8
Dimethylnaphthalenes	2.0
Acenaphthene	9.0
Dibenzofuran	5.0
Fluorene	10.0
Methylfluorenes	3.0
Phenanthrene	21.0
Anthracene	2.0
Carbazole	2.0
Methylphenanthrenes	3.0
Methylanthracenes	4.0
Fluoranthene	10.0
Pyrene	8.5
Benzofluorenes	2.0
Chrysene	3.0

not identified (168). Ozone also appears to oxidize PAH's, but products have not been identified (168, 171, 172). Although hypochlorous acid reacts with biphenyls (48), the chlorinated biphenyls produced are toxic (67).

Creosote constituents are also photochemically reactive (173). Photochemical products of benzpyrene in aqueous solution were identified as oxidized derivatives, but the product toxicity has not been described.

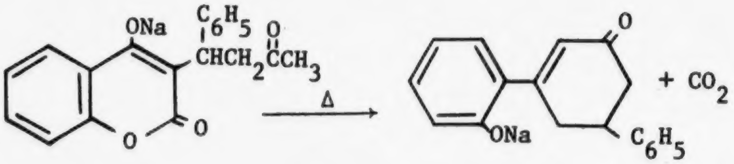
Empty containers should be thoroughly drained before disposal. Water will not be effective for container rinsing. Creosote is normally used without dilution, so rinse with kerosene or other hydrocarbon solvents would leave the rinsate as a disposal problem.

In summary, there is no suitable means of chemically degrading creosote. Creosote and its containers should be disposed by the EPA recommended procedures (Section 3) (7a).

E.4 CHEMICAL METHODS FOR DETOXIFICATION OF WARFARIN

Warfarin is an anti-coagulent rodenticide and also an anti-coagulent drug for humans. Warfarin, a hydroxycoumarin has an acidic group. While the free acid is slightly water soluble (4 mg/100 ml at 30°C), alkali salts are water soluble (115). Aqueous solutions of the sodium salt, warfarin sodium, are also used as rodenticides. Warfarin is formulated as a bait concentrate of 0.5% in cornstarch, as finished baits of 0.025 to 0.05%, and as a 1% dust. Warfarin sodium is available as a 40% (W/W) aqueous solution (15, 104).

Warfarin structure has two ketone groups in addition to the acidic enol group. Its chemistry consists of reactions typical of enolic alcohols and ketones. The enolic group reacts with alkylating agents, such as diazomethane and acyl chlorides to yield ethers and esters. It forms typical keto-derivatives. When it is warmed in methanol containing acid catalysts, such as anhydrous hydrogen chloride, it forms a ketal. Imines are formed with amine derivatives; for example, it forms hydrazones with hydrazine derivatives. Warfarin rearranges when heated in aqueous alkali (105).



Warfarin and its containers should be disposed according the the EPA recommended procedures (Section 3) (7a). If land disposed, warfarin sodium leaching could be reduced when it is acidified and converted to the less soluble acid form (175).

APPENDIX F

PESTICIDE CONTAINER RINSE PROCEDURES

Before an empty glass or metal container is either destroyed and buried or is sent for recycling, residual pesticide should be removed (1, 2). The companion Handbook for Pesticide Disposal by Common Chemical Methods has recommended the NACA triple-rinse procedure. And, for pesticides which are susceptible to detoxification by alkaline hydrolysis, it recommended rinse with a caustic decontaminant. Recent studies on container rinse and decontamination suggest some modification of their recommendations. This section reviews salient studies.

Research at Oregon State University evaluated residue removal from 5, 30, and 55 gallon containers at a drum recycling plant (176, 177). They compared residue removal by triple rinse with water; plant processing which included caustic rinse and immersion into caustic (1-2% sodium hydroxide) at 200°C; and a combination of the two methods. Triple rinsing effectively removed the residues of formulated pesticides (including phorate, disulfoton, chlordane, 2,4-D, and diazinon). The triple rinse generally removed 80% or more residue. Slightly better reduction was achieved with caustic rinse. The OSU group suggested that pesticide residues are removed by dissolution in water, hydrolysis, and other processes. Residue fate in the caustic rinse was related to the rate of hydrolysis: carbaryl degraded completely within 30 minutes; diazinon had an observed half-life of 21 hours; partial degradation was observed for disulfoton; but chlordane did not degrade.

The OSU study demonstrated inherent variation in residue reduction efficiency. Triple rinsing (water) left the following median and range of residues in 55 gallon

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drums: phorate - 8.63 g, 3.98-15.20 g; chlordane - 3.10 g, 1.25-8.34 g; 2,4-D - 4.76, 0.86-10.90 g; and 2,4,5-T - 7.2 g, 1.67-21.71 g. Also, in a series of 10 55 gallon phorate drums treated by a combination of triple rinse and caustic processing, the residue reduction ranged from 77 to 95% in 9 barrels but only 37% in one barrel. The results indicate that although rinse is effective, occasional drums could retain significantly larger residues. They suggested one source of the variation might arise since a high percentage of the residue (81%) was within the barrel chime (rim).

Archer evaluated the removal of 2,4-D residues from 5, 30, and 55 gallon metal drums by rinses either with water or ethanol-acid (178). Concentrates of 2,4-D formulated as alkanolamine salts and as propylene glycol butyl ether esters were examined. Simulated residues were produced by adding the estimated volume which would be retained after completely draining the container. Table 34 summarizes salient data. Triple rinse with ethanol-acid removed more residues of the ester formulation than water rinse. A single ethanol-acid rinse removed more of the alkanolamine salt than water, but with triple rinsing the differences between the two solvents are small.

Hsieh and coworkers evaluated the residue removal and chemical degradation of parathion formulated as the 4 lb/gal emulsifiable concentrate (53). They examined residue reduction in glass bottles (125 ml and 1 gallon) and 1 gallon epoxy coated metal drums by rinsing with three solvents: water; alkaline detergent (pH 12.45); and DIAS (250 g of disodium dioctylsulfosuccinate, 50 g of sodium valerate, 50 g of sodium caprylate, 90 g of ethylene glycol, 80 g of sodium carbonate and 8 g of sodium silicate in 1 liter of water then diluted twentyfold - pH 9.88). Wash volumes were 25 ml for 125 ml glass bottles, 75 ml

Table 34. Removal of 2,4-D from Metal Containers by Rinse with Water or Ethanol-acid. Adapted from Archer (178).

2,4-D Formulation	Rinse Solvent	Number of Rinses	% Residue Reduction 5 gallon drum[a]	30 gallon drum[b]	55 gallon drum[c]
Alkanolamine Salt	Water	1	88.6	87.7	85.6
Alkanolamine Salt	Water	3	94.6	97.5	99.3
Alkanolamine Salt	Water	8	95.1	98.5	99.6
Alkanolamine Salt	Ethanol-acid	1	95.3	98.7	99.7
Alkanolamine Salt	Ethanol-acid	3	95.4	98.8	99.7
Propyleneglycol butyl ether esters	Water	1	--	54.9	70.3
	Water	3	--	82.5	89.9
	Water	4	--	--	91.8
	Water	8	--	94.9	--
	Ethanol-acid	1	--	97.3	94.3
	Ethanol-acid	3	--	99.0	95.5

(a) Rinse volume is 250 ml.
(b) Rinse volume is 750 ml.
(c) Rinse volume is 1000 ml.

for 1 gallon glass jugs and 150 ml for 1 gallon steel drums. Initial rinse removed about 98 to 99% of the residues from all containers except the metal drums; no differences between solvents were found. A single water rinse removed only 88% from the metal drum. Three water rinses removed 98% of the residue from the steel drum and about 99% from the glass containers.

They evaluated hydrolysis rate of parathion by 1N sodium hydroxide. Table 35 summarizes salient details. The parathion is hydrolyzed very slowly by aqueous alkali. The rate is accelerated by sodium hypochlorite (NaOCl), which apparently oxidizes the parathion to paraoxon (see Appendix A-11). Ethanol decreased the hydrolysis time. They explained that when parathion is in the aqueous medium it remains emulsified, but to hydrolyze it must be in solution (see Appendix A-1). The ethanol serves to dissolve the parathion.

Table 35. Effect of Ethanol and Hypochlorite on the Hydrolysis of Parathion in 1N NaOH Solutions. Adapted from Hsieh et al. (53).

		Residual Parathion %[a]		
Additive	Conc. %	5 hours	10 hours	26 hours
None	0	94.9	90.6	84.7
	25	78.9	59.0	32.7
Ethanol	50	87	ND[b]	ND[b]
Sodium hypochlorite	2.62	66.4	61.6	35.0

(a) Initial parathion concentrations ranged from 927 to 982 ppm.
(b) Not detected.

In conclusion, triple rinsing will effectively reduce pesticide residues in empty, drained containers. The residue reduction for pesticides of low solubility will be assisted by adding ethanol to the wash solvent. Chemical hydrolysis of the residues requires the pesticide to be dissolved. This significantly affects the residue reduction for pesticides with a low aqueous solubility, such as parathion and diazinon. For this reason caustic in 50% aqueous ethanol is suggested as the wash solvent for containers of those pesticides of low water solubility and moderate hydrolysis rate.

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